Novel Methods and Materials in Development of Liquid Carrier Membranes
From the Molecule to the Process

Von der Fakultät für Maschinenwesen der Rheinisch-Westfälischen Technischen Hochschule Aachen zur Erlangung des akademischen Grades eines Doktors der Ingenieurwissenschaften genehmigte Dissertation

vorgelegt von

Diplom-Ingenieur Mitja Medved
aus Maribor, Slowenien

Berichter: Universitätsprofessor Dr.-Ing. Thomas Melin
Universitätsprofessor Dr.rer.nat. Marcel Liauw


Diese Dissertation ist auf den Internetseiten der Hochschulbibliothek der RWTH Aachen online verfügbar.
Acknowledgements

The booklet at hand is a product of my last seven years’ intense learning, research and other activities conducted within the frame of Institut für Verfahrenstechnik (IVT) at Aachen University of Technology. Throughout this period, in which sometimes the work load appeared to never end, I was luckily surrounded with friendly but also knowledgeable people. Among them, special thanks goes to those who helped me pull through all the challenges placed in front of me.

Firstly, I appreciate the endeavors of my doctoral advisor Prof. Dr.-Ing. Thomas Melin for his supporting and encouraging supervision. I could not have imagined having a better mentor and advisor, giving me all the (academic) freedom needed for my professional and personal development.

I would like to thank Prof. Dr.rer.nat. Marcel Liauw, who critically and thoroughly took over the revision of the thesis as the second advisor.

Many thanks to Mr. Prof. Dr.rer.nat. Peter Wasserscheid, who brought in the idea of using ionic liquids in membrane separations and provided them to us directly from his labs. Without him the thesis would definitely concern another research topic.

Some aspects of my work were treated by the students of chemical engineering at IVT that I supervised as good as I could. In spite of never having really trusted their results, I am greatly indebted to their contributions. Special credits go to Anand Sundararajan, Alexander Bischert, Daniel Becker and Clemens Fritzmann.

Much respect deserve my office mate and friend Andreas Nattkemper for putting up with me and for finding the right words at the right moments. Jochen Küntzel contributed an extra something to the cheerful working atmosphere in our office. Sharing ideas with Jens Hoppe stigmatised my brain forever and without him I would certainly be someone else. A special thanks deserve my successor at the institute Florian Krull for helping me with the final experiments.

Thanks also to all other colleagues and coworkers of the institute from the lab, both workshops and secretariat.

And finally, I cannot overstate my gratitude to my longtime companion Ela and her daughter Katharina, who helped me find an answer to the one of the most important questions arising in one’s life: Have I ever really loved? It is a great mercy to be able to answer this in the affirmative.
O ME! O life! . . . of the questions of these recurring;
Of the endless trains of the faithless — of cities fill’d with the foolish;
Of myself forever reproaching myself, (for who more foolish than I, and who more faithless?)
Of eyes that vainly crave the light — of the objects mean — of the struggle ever renew’d;
Of the poor results of all — of the plodding and sordid crowds I see around me;
Of the empty and useless years of the rest — with the rest me interwined;
The question, O me! so sad, recurring — What good amid these, O me, O life?

Answer.

That you are here — that life exists, and identity;
That the powerful play goes on, and you will contribute a verse.

Walt Whitman (1819-1892)
To my parents

For not answering all my questions and...

...for making me seek the answers by myself instead.
Preface

Back in 1999, my alternative civilian service approaching its end, I was looking for a job. For some innate reason I was focusing pharmaceutical industry only. I have to admit that at that time I already had a very ambitious wish to continue my education carrier within the frame of PhD studies in the industry. Therefore, I was looking for an advisor, who would take over the supervision of my work. I led quite long e-mail correspondence with Prof. Melin whom I knew from Bayer AG, where I did my first industrial working experience in summer 1996. Meanwhile, I got a position in a big pharmaceutical company in Slovenia. But then Prof. Melin suggested that it would be much more reasonable to do the research work at the university and proceed for industry afterwards. He invited me to Aachen and I quickly decided to follow that call to Germany.

I can well recall my first serious conversation about my future tasks at IVT with Prof. Melin. It was clear that I would become the member of the „fabulous” membrane group working on gas and vapour separations with membranes. In the beginning, I should have worked on the improvement of inorganic membranes, in particular in pin-hole closure of zeolite and silica membranes using procedure called „opposing reactants geometry” [1]. After less than a few months of literature review it proved almost impossible to do proper work without having a clean room [2]. This installation was clearly too expensive for the current financial situation. We therefore considered a research project on conducting selective catalytic reactions on an in the zeolite membranes [3], but must had realised soon that prospects were rather poor. Another very interesting topic in question was modification of zeolite membranes according to the „ship in a bottle”-principle [4]. However, apart from expected deficient occupancy of zeolite cages by the carrier, we would need quite a few dozens of scarce, commercially non-available Y-zeolite membranes. The producer of these membranes was not only in financial troubles but also had manufacturing problems. Abandoning this option, we envisaged the liquid carrier membrane concept. I wanted to approach the problem of nitrogen-oxygen separation from unusual perspective: perfluorocarbons (e.g. perflourooctylbromide) were, based on the famous submerged mouse-experiment [5], currently also discussed in medical science as temporary intravenous blood substitutes [6, 7]. Intrinsic oxygen solubility of these oxygen carriers proved to be excitingly high [8]. Due to their surfactant properties they were also suggested for nonconventional therapy known as liquid ventilation [9]. They were even considered as fermentation medium in biotechnology [10]. In spite of these advantages, perfluorocarbons show considerable vapour pressure and are therefore of limited value in gas and vapour separation by supported liquid (carrier) membranes. Luckily, at this time, Mr. Prof. Wasserscheid introduced us ionic liquids, which appeared to be very
promising solvents for development of new and for improvement of existing membranes. We changed our plans a little bit, working area, however, remained „liquid membranes” and „facilitated transport liquid membranes”, and bought fume cupboard for chemical syntheses and experiments. All the equipment was then put into the pilot plant area of the institute. This chemical corner, recently equipped with two glove-boxes, is still a very funny, almost exotic sight among other robust engineering equipment placed there.

During the years of research, some other ideas not having much in common with my primary thesis work were generated. One brainchild here and another there led into quite time consuming proposal writing: without a „bunch of bucks” no research can be done. There were proposals on microreactors, on membrane reactor and two on molecular modelling - one in the field of crystallisation and another in the field of mass transport modelling in zeolite membranes. At least the last topic, molecular modelling, proved to be a real advantage for my own work. Writing proposals, however, had an important side effect: I did realise how difficult it is to drag money out of other people’s pockets. Looking back at this work, I am somehow proud of all the running projects I have been able to initiate, providing ideas and work for new people to come after me.

Many of those „creative” ideas came into being while attending workshops and conferences (e.g. ICCMR 2000 Zaragoza, Spain; ICOM 2002 Toulouse, France). I am very grateful for this continuous policy of IVT, which enabled me in participating these scientific meetings. At several places I was also able to present my own work in the form of oral presentations (e.g. ECCE 2001 Nuremberg, Germany) or in the form of posters (e.g. SSCHI 2001 T. Matliare, Slovakia).

Worth mentioning is in particular the team project of the whole membrane group at IVT called „the membrane book” [11], where I contributed material for two chapters (Membrane structures, materials and manufacturing; Electrodialysis). My own experience in the field of inorganic membranes together with gathered information from the literature (as required for the book and as collected in this thesis), from the internet (e.g. [12]) and personal communications let me become a bit of material scientist as well and helped me in the line of reasoning throughout the PhD studies.

Fortunately, I also had many opportunities to cooperate with departments of big chemical companies, especially Bayer AG (Leverkusen) and could attend some very instructive meetings with people from the industry (Shell, Air Products, Dräger). Useful contacts with industrial partners induced partial financial support of this thesis: in one project we worked for the company Creavis (Degussa Group, Marl) for about a half a year. Companies HITK (Hermsdorf), Mann&Hummel (Ludwigsburg) and Pall-Schumacher (Crailsheim) kindly provided their materials for my research and through their support they showed at least some interest in my work.

In my opinion, the primary function of the university is not the research itself, but to act as a high-quality educational institution. In this sense, I tried to pursue my teaching duties as seriously as possible. Because of these endeavours and due to the massive support from my colleagues, we were able to establish an effective and sustainable data-management system, which enabled us a continuous improvement of existing knowledge and teaching methods. Looking back, I can say now that for me teaching [13] was one of the more, if
Finally, I find it necessary to answer the question what is working on PhD good for? Firstly, it is the great opportunity to feel how it is, when your old and also just newly acquired knowledge and abilities approach their capacity limits. Secondly, the main issue seems to be overcoming the arising frustrations of every kind, since experimental work can be as difficult as modelling and conducting simulations on computer. However, relativising this, it is good to keep in mind that current models on the physical reality are models only, otherwise they would be the thing itself [14]. Thirdly, yet another aspect is also to learn how to cope and work with people you do not really like. But this would probably happen in any working environment’s collective. In this aspect, one of the important lessons I obtained is, that in order to aim at success, one needs people, a team, of very diverse skills and abilities. If people share visions, they are more likely to be really motivated and each one will be willing to contribute his or her part to the common goal.

Finally, the last introductory words: The goal of profoundly covering everything from quantum mechanics to technical applications in the thesis - expectedly - turned out to be too high flying. I was warned not to try to write an overcomplete thesis, since a good racing horse should never jump higher than necessary! I think I was not jumping to high - sometimes maybe just in wrong directions. I am well aware that in the field of science and technology completeness can never be claimed. So, even if I wished I did, how could I possibly have written a complete thesis?

Research work makes me reflect the story of “digging the planet”: one has to decide whether one wants to dig the surface or to make a deep tunnel. In both cases, the amount of moved material is the same. But what is essentially different is the perspective. I have consciously chosen the surface and in this sense, I tried to avoid any kind of scientific „l’art pour l’artism” and targeted rather at what I believed to be pragmatic and practical aspects. In some chapters I allowed myself subject directed polemics, with an aim to reveal deficiencies in both methods and thinking. These might be then considered to be the starting ground for the future research.

I hope I could provide readable, enjoyable and perhaps even useful thesis.
## Contents

1 Thesis’ Context .......................................................... 1
   1.1 On Membranes ...................................................... 1
       1.1.1 Dense Membranes .......................................... 2
       1.1.2 Membranes in Chemical Reaction Engineering ........ 4
   1.2 Motivation: Needs or Trends, Both or What? ............... 6
       1.2.1 Why liquid membranes? .................................. 8
   1.3 An Outline of the Thesis ....................................... 8

2 Introduction ............................................................ 11
   2.1 Miniaturizing of Processes ...................................... 11
   2.2 Liquid Membranes ................................................ 14
       2.2.1 Biological Membranes ................................... 14
       2.2.2 Simple Liquid Membranes ................................ 15
       2.2.3 Carrier Membranes ...................................... 16
   2.3 Quantities that Determine the Behavior of SLM ............ 18
   2.4 Mass Transport Review .......................................... 20
   2.5 Summary of Thesis’ Context and of Introduction .......... 22

3 Mass Transport Modelling ........................................... 23
   3.1 Introductory definitions ........................................ 23
   3.2 Simple Model ..................................................... 25
       3.2.1 Facilitation Factor and Permeate Flux ................. 25
       3.2.2 Case study details and results .......................... 25
   3.3 Complex Model ................................................... 30
       3.3.1 Membrane Module: Geometry, Carrier Reaction, Operating Conditions ........................................... 30
       3.3.2 Modelling .................................................... 32
       3.3.3 Implementation in Femlab ................................. 47
3.3.4 Mass Transfer Simulation - Results .................................. 51
3.3.5 Conclusions on Simulations ........................................ 57
3.4 On chemical equilibrium .................................................. 57
  3.4.1 Enthalpy of Reaction ................................................ 58
  3.4.2 Gibbs Free Energy and Chemical Potential ...................... 59
  3.4.3 Equilibrium Constant .............................................. 61
3.5 Summary ........................................................................... 64

4 Molecular Modelling ......................................................... 65
  4.1 Introductory remark ....................................................... 65
    4.1.1 Software .......................................................... 66
    4.1.2 General procedures in molecular modelling .................. 67
  4.2 Known Carriers ............................................................ 68
    4.2.1 Carriers for Oxygen ............................................... 68
    4.2.2 Carriers for Olefins .............................................. 85
  4.3 Computationally Designed Carriers ................................... 99
    4.3.1 Modification of Salen by Metals Rh and Ir .................. 99
    4.3.2 Quantum Chemical Treatment of Group (VI)-rhenates ...... 100
    4.3.3 Ionic liquids as carriers? ........................................ 102
    4.3.4 Dicationic Olefin Ni(II), Pd(II) and Pt(II) Complexes .... 103
    4.3.5 Carriers for carbon dioxide ..................................... 105
    4.3.6 Other carriers .................................................... 107
    4.3.7 Solvent effects on solutes solubility .......................... 107
  4.4 Process parameters from molecular modelling ...................... 111
    4.4.1 Calculations of gas and vapour solubilities in ionic liquids 111
    4.4.2 Diffusion coefficients in ionic liquids ....................... 114
  4.5 Conclusions .............................................................. 122

5 Materials and Experimental ............................................... 125
  5.1 Ionic Liquids ............................................................. 125
    5.1.1 How Special are Ionic Liquids? ............................... 126
    5.1.2 Ionic Liquids Used in the Thesis ............................. 127
    5.1.3 Properties of Neat Ionic Liquids ............................. 128
    5.1.4 Viscosity and density .......................................... 128
    5.1.5 Relative permittivity ........................................... 129
    5.1.6 Solubility of Gases and Vapours in Neat ILs ................ 131
1 Thesis’ Context

Development and production of any product of continuously increasing quality, especially of consumer goods, is only possible by applying appropriate high-quality raw and supporting materials. Market requirements for better products are ever ascending and therefore the production of pure chemicals must comply with these demands. Downstream, in particular separation technologies in the feedstock industry together with separations implemented for environmental protection often make up the core of the production processes and are usually very cost-intensive. Therefore, an industrial engineer is faced with the great and constant needs for the improvement of existing separation methods, making them cheaper and more efficient.

Membrane technology has proven not to be only an attractive subject of academic research. Membranes separations have, in addition to classical separations like distillation, extraction, absorption, adsorption, crystallisation and filtration, become largely established in the industry over the last four decades. Its practical relevance is evidenced by the appearance of thorough reviews in the engineering literature [15, 16], the coverage of this field in several monographs [17, 18, 19, 20] as well as by increasing number of research articles and patents. The most striking evidence for the importance and diversity of the membrane technology is perhaps the review on the „Relevant books for membranologists“ [21], a compilation of more than 450 books concerning only human-made membranes (biological membranes being a domain of biochemistry and cell biology). Membranologists, who annually organise several conferences devoted exclusively to membranes and applications connected with them, have since 1976 even their own journal, The Journal of Membrane Science. However, membrane science related issues are, of course, widely published elsewhere, too.

In the following sections the field of membranes and closely related (alternative) separations is shortly reviewed in order to put the subject of this work, i.e. liquid membranes and liquid carrier membranes, into the right context.

1.1 On Membranes

In principle, two big groups of membranes can be distinguished: porous and non-porous or dense membranes (Fig. 1.1). Membranes with a porous structure are used in microfiltration and in ultrafiltration. They are made of either organic or inorganic materials, which themselves generally do not influence the mode or the quality of separation. The size of the retained particles depends exclusively on the pore size distribution of the given membrane and even more on the properties of the cake formed on the membrane surface,
which actually acts as a separation layer during the separation process. Whereas the porous membranes can be considered to be only an improvement of the early classical filters [22], the separation performance of so-called dense membranes has today surpassed the benchmark of simple filtration of particulate matter by enabling separations well down into the molecular level.

1.1.1 Dense Membranes

According to the material of the active layer of the given membrane (only exemplary references are given here), several categories of dense membranes can be distinguished:

- polymer membranes [23, 24].

Figure 1.1: Different membrane types: a) porous polypropylene membrane (PURON AG); b) porous aluminium membrane (GAP AG); c) dense organic composite reverse osmosis membrane (ROCHEM); d) dense inorganic membrane (HITK). The first two membranes are symmetric and do not pose an extra separation layer as do the latter, asymmetric ones.

In dense membranes that are used in pervaporation, gas and vapour permeation, electrodialysis and partly in nanofiltration, the careful choice of the membrane material and its intrinsic material properties is essential for achieving high quality separation performance. In these cases, chemical species to be separated from the feed mixture interact directly with the molecules in the separation layer of the membrane. For example, surface charges are, due to the presence of the charged groups within the separation layer of the membrane, of great importance in nanofiltration and electrodialysis. Furthermore, dipole and van der Waals interactions strongly influence the solubility and diffusivity (i.e. mobility) in most of the known membrane matrices.
1.1. ON MEMBRANES

- liquid membranes [25],
- ceramic (perovskite, silica) membranes [26, 27],
- metal (palladium-nickel-silver) membranes [28, 29],
- zeolite membranes [30] and
- carbon (molecular sieves, CSM) membranes [31].

Although e.g. silica, zeolite and CMS membranes, where the actual pores are of molecular dimensions, can in principle be seen as porous membranes, the question, when the pore is big enough to be considered a pore, is rather philosophical. In this light, the boundary between the porous and dense membranes appears somehow arbitrary. However, it can be stated here that all these (ideal) dense membranes share the same basic principle of mass transport, whereupon generally applicable solution-diffusion model is based [32]. Mathematically formulated relationships may differ from case to case, depending on the very details of the respective postulated mass transport mechanism (cf. [11]). Nevertheless, there are three phenomenological steps that are crucial for a component to be transported through the dense membrane:

- (ad-, chemi- or physi-)sorption into the membrane through the feed membrane surface,
- (activated) diffusion or „hopping” through the membrane phase and
- desorption from the membrane through the permeate membrane surface.

Each step can be individually described in order to decently represent the observed, i.e. measured data and so to meet the engineering needs.

In contrast, modified and refined filtration models (based on Carman-Kozeny equation) are used for the description of mass transport through porous membranes [11].

In the following, liquid membranes, being the subject of this work, are shortly discussed.

**Liquid Membranes**

Thus, liquid membranes [33] belong into the group of dense membranes. The term „liquid membrane” is closely related to the processes of membrane supported extraction that are called „pertraction processes”. The term basically refers to at least (cf. [34]) three different arrangements that have been in use in practise and in research [35]: emulsion membranes, membrane contactors\(^1\) and immobilised liquid membranes (ILM). Schemes of emulsion liquid membrane and of immobilised liquid membrane are, according to [11], shown in Fig. 1.2.

\(^{1}\)Liquid membrane contactors (MC) are usually treated separately from other types of liquid membranes and therefore I will stick to this silent agreement.
1. THESIS’ CONTEXT

1.1 Membranes in the Theses’ Context

1.1.1 Liquid Membranes in the Theses’ Context

Figure 1.2: Schemes of liquid membranes in the constellation of: a) an emulsion (with phase dispersion); b) an immobilised lamellae (without phase dispersion)

Since we will not encounter emulsion liquid membranes (ELM) in further text, here only a few words about them. ELM are actually one variant of the more common industrial arrangement of the extraction process based on the mixer-settler principle. The main difference exists in the application of emulsifiers that are used for the stabilisation of the phase boundaries of the emulsion within the emulsion. The outer phase is the donor solution and the most inner emulsified phase is the acceptor solution. Both phases are brought into the contact through the liquid membrane phase, which is immiscible with both other phases and separates them. The final emulsion in equilibrium, however, must not be too stable itself, since the extracted species must be discharged from the acceptor phase by emulsion breakage. The acceptor phase is collected from the inner phase, then discharged and recycled for the preparation of the new emulsion, which can in turn be used for another (reactive) extraction cycle. This arrangement is only applicable to liquid systems\(^2\) [36] and the major drawbacks are its energy intensive mode of operation and phase-losses due to the unavoidable partial phase miscibility.

Supported or immobilised liquid membranes are dealt with within this thesis. They can be considered to be hybrid membranes being build of a thin organic or inorganic porous support and of a carefully chosen liquid that is trapped in the pores of the support and held there by capillary forces. In this constellation, the liquid in the support builds up thin lamellae and in this way becomes a membrane. As in ELM, membrane building liquid acts as an extraction medium preferably for a single component of the feed mixture. In contrast to ELM, ILM can be used for liquid-liquid as well as for gas and vapour separations. We will return to the treatment of liquid membranes (both ILMs and MCs) in more detail again in Chapter 2 after I have dealt with the application of membranes in the chemical reaction engineering.

1.1.2 Membranes in Chemical Reaction Engineering

Performance enhancement of the classical unit operation techniques can be done by combining them with selective reactions. Reactive separations [37] are not new: reactive

\(^2\)The majority of liquid membranes for liquid-liquid extraction have been used for extraction of heavy metal ions from aqueous waste streams.
1.1. ON MEMBRANES

absorption and reactive (catalytic) distillation are known for decades and are well commercialised. Other reactive separation processes include reactive extraction, reactive adsorption, reactive crystallisation and finally, reactive membrane separation.

In the context of the membrane usage for conducting chemical reactions, one has to have in mind the basic differences between membrane reactors and reactive membranes [38, 39, 40]. Both can be used as a means for chemicals separation as well as for their production. In the literature, one often finds these terms used in idiosyncratic manner [41]. The confusion probably arises because in most cases, i.e processes, catalyst is required and its presence in the referred reaction apparatuses leads to the umbrella term „catalytic membranes” [42, 43]. Materials used in catalytic membrane applications do not differ from the materials used in their classical counterparts, except for their geometrical arrangement and for the presence of (dense) selective membrane layer.

Generally speaking, membrane reactors integrate the reaction and the separation step into a single device, thereby miniaturising the overall process. The reaction and separation steps nevertheless take place at different locations within the device [44]. Basically, two types of membrane reactors can be distinguished: the first type suits for shifting the equilibrium from the left to the right in the following exemplary equilibrium reaction

\[ A + B \rightleftharpoons C + D \]

by withdrawal of one, usually not desired byproduct from the product mixture through the membrane (Fig. 1.3a, thereby yielding higher conversion with respect to the desired product.

In order to increase the selectivity in consecutive reactions

\[
\begin{align*}
A + B & \rightarrow C, \\
C + B & \rightarrow D,
\end{align*}
\]

C being the desired product, these can be treated in the second type of membrane reactor in two manners. The intermediate product C can be either selectively removed in-situ or one reactant is added in a controlled manner through the membrane preventing the subsequent reaction taking place. In the later case, in contrary to the equilibrium reactions, membranes used must not necessarily be selective (Fig. 1.3b.

Reactive membranes, on the other hand, are catalytically active themselves, i.e. reaction and separation both take place simultaneously in the active layer of the membrane. Whereas the concept of membrane reactors as devices is experimentally more or less straightforward, dealing with „real” reactive membranes is more complicated. According to whether the catalytic reaction conducted within the reactive membrane is irreversible or reversible, membrane reactors with reactive membranes and carrier membranes can be distinguished, respectively (Fig. 1.3c and d).

With the exception of reactive biomembranes, where on the selective membrane support layer biofilms of immobilised enzymes or microorganisms are formed [45, 46, 47], comparably little work (e.g. [48, 49, 50, 51]) has been performed on irreversible reactions.
In contrast, research work on carrier membranes, which can definitely be assigned to the reactive membranes\(^3\), has a very long academic record, which is evidenced by innumerable hits in the on-line chemical abstracts service (CAS, Sci-Finder). Carrier membranes in constellation of liquid membranes, being the subject of the thesis, will be dealt in more detail in Chapter 2.

More introductory information on further possible membrane classifications and on membrane technology in general is available in [52, 53].

### 1.2 Motivation: Needs or Trends, Both or What?

In academic publications, tackling problems of supposedly industrial or environmental importance is often claimed to be the motivation for the research and development - the field of membrane processes is no exception to this trend.

Increasing carbon dioxide concentration in the atmosphere [54] should have invoked many research projects on carbon dioxide separation with membranes in order to reduce the greenhouse effect (sequestration). The same also holds for the membrane applications in the earth gas sweetening, i.e. in the removal of CO\(_2\), SO\(_2\) and H\(_2\)S from their mixtures with methane [55]. Downstream processing of C\(_2\) and C\(_3\) hydrocarbons produced by steam and catalytic cracking of naphta is yet another example. Ethylene and its coupled by-product propylene are the largest-volume petrochemicals worldwide with a production of more than 70·10\(^6\) t/a and 30·10\(^6\) t/a, respectively [56]. The distillation of C\(_2\) and C\(_3\) fractions under pressure having large energy consumption, there is an enormous economic incentive [57] to develop cheaper alternative separation processes, e.g. based on membranes.

Are the claims on the motivation above legitimate? Can they really be the motivation for the academic research? Can academic research provide new alternative technologies? What can actually be the contribution of the academic research?

---

\(^3\)It is reasonable to consider a carrier as a catalyst.
1.2. MOTIVATION: NEEDS OR TRENDS, BOTH OR WHAT?

Firstly, which company would, for the sake of public opinion, allow itself admitting that it has any kind of problems? One can consequently expect that the actual problems and needs for their solutions will remain hidden. The situation is rather unclear and motivation claims are thus questionable. One also should have in mind that working industrial solutions for the given tasks, whatever deficient, already exist (at least those already being in use) and that operating engineers steadily work on the improvements of the running processes. Furthermore, research efforts within big companies are usually well founded [58] and very goal directed. Honestly, academic research is financially no match for industrial research [59]. When going through the patent literature, this may lead to frustrations instead to the motivation, for a lot of work has already been done and a lot of ideas have already been patented. New solutions and technological proposals, in order to be industrially relevant, must significantly out-compete existing technologies from both ecological and economical point of view (low investment costs, short-term break-even point and less environmental impact, i.e. emissions, etc.). As a typical example might serve the production of propylene oxide by two methods, by chlorohydrin process and by indirect oxidation route (peroxidation) [60], where the unambiguously better solution with indirect oxidation still did not replace the old technology [61]. Even if academic research can provide some solutions, it might take years for their implementation. New products like membranes or processes based on membrane technology have long found no acceptance by rather conservative engineering staff in the production divisions of big chemical companies.

Moreover, academic research usually does not provide sufficiently robust solutions for chemicals separation or their production. Feasibility of scale-up is often not considered - even in cases of the bulk chemicals production. Many brilliant new ideas are mostly deficient in respect to this issue [62]. As an example, the usage of carboanhydrase enzyme [63] in an absorptive CO\textsubscript{2} removal from the exhaust gases of power plants driven by incineration of fossil fuels can be mentioned. The enzyme works as an indirect accelerator for CO\textsubscript{2} transport across gas-liquid phase boundary by catalysing the reaction of CO\textsubscript{2} with water in the bulk phase, which is thought of as a thermodynamically slow and also quite delicate in respect to CO\textsubscript{2} partial pressure, pH value and temperature. The amounts of gaseous materials to be treated are enormous and crucially required absorption capacity of water is, even when the system is in the equilibrium state, physically not given. The same idea transferred to a carrier membrane system [64] promises at least a commercial development of a feasible process, that might be useful for small scale separations [65].

In academic research, the first question before aiming at development of e.g. novel separations by membranes or at development of membranes themselves should not concern the market for membranes or market’s needs for any desired final product. It also should not focus the estimation of the potential financial costs [66, 67] for the implementation of the given applications.

In my opinion, academic research can not compete with industrial research in many respects and actually, it should not. Ideally, it should be in the service of mankind generating public domain knowledge in the fields of development, improvement and refinement of scientific methods as tools. Academic non-profit research must therefore follow innovative credo by realisation of exploratory concepts.
In this thesis, some of the materials and the methods used are completely new or new in the given context. Apart from some principal and well known classical approaches, I have decided to provide as broad scope of concepts in the development of liquid carrier membranes as possible, with an ultimate goal of knowledge integration from many fields. This daring goal is my motivation and it is presented in the following thesis’ outline.

1.2.1 Why liquid membranes?

Although there are some promising results regarding selectivity and flux, the development stage of liquid membranes is far from that of conventional (polymer) membranes. Liquid membranes therefore cannot compete with established membrane on the large scale. In fact, there have been only very few pilot plants reported, which have used liquid membrane technology and most of them have been abandoned because of their insufficient results, especially with respect to poor long term stability. However, research on liquid membranes has been kept alive, the main reason being the enormous potential in case of breakthrough [68]. Experimental challenges in a laboratory scale comprise primarily the production of very thin membranes with long time stabilities and durabilities under different operational conditions. Furthermore, the research in the field of thin reactive films is of great theoretical interest: it focuses the fundamentals of the mass transport and of the reaction phenomena, which can be generally extended to other processes.

1.3 An Outline of the Thesis

In the past, a multitude of dense membranes including liquid membranes, especially those with incorporated carriers, have been exploited. Therefore, the inclusion of an extra introductory chapter, Chapter 2, on the course of development, the separation approach strategies with carrier membranes and the state of the art in this field appears necessary. The underlying notions that hold for carrier membranes in general, and for liquid carrier membranes in particular, will be elucidated. Existing mass transport models will be shortly reviewed.

The review from the Chapter 2 should act as the starting point for the Chapter 3, where mass transport in liquid membranes - as they have been produced and partially examined in the experimental part of this thesis - will be treated theoretically by the means of classical model set-up implemented in the numerical simulation software. Setting up a model, whatever simple, is necessary for understanding of the separation operation principles. Mathematical treatment of the carrier membrane system provides an access to the information on the desired properties of the potential carrier under relevant technical conditions. In principle, for a given carrier, optimum operation conditions can also be calculated theoretically. In particular, requirements on thermodynamics and kinetics of the carrier system will be under consideration.

The scope of existing carriers that might be used for facilitation of mass transport through liquid membranes is, however, quite limited. Therefore, the search for the novel carriers is important in the development and improvement of carrier membranes. Today, quantum
mechanics methods can, as a tool, help in accomplishment of this task. The main question
is, by knowing the most probable operating conditions, how to design a carrier with desired
properties or how to identify potential carrier among proposed compounds, for which the
search strategies are still more or less dependant on „chemical intuition“. Within Chapter
4, being the main focus of this thesis, firstly, known carriers will be treated with different
molecular modelling approaches. Subsequently, potential carriers will be evaluated in the
same manner. Some molecular modelling techniques other than quantum mechanics will
also be used for acquisition of crucial process parameters, which play an important role
in liquid carrier membranes.

Finally, in Chapter 5, more or less stand-alone experimental work and work based on
considerations from Chapters 3 and 4 will be presented and discussed. In this chapter,
investigations on novel materials used in the thesis, especially on ionic liquids, porous
supports, carriers and combination thereof in the form of liquid membranes will be de-
scribed. The necessary theoretical background to materials, their properties and to each
experimental topic will also be given here. Interrelationships of theoretical considera-
tions and experimental phenomena will be disclosed in the interpretation of permeation
experiments.

Condensed results will be presented in Chapter 6, where an outlook will also be given.

In appendices, I have included information that I thought to be useful for an engineer
working in the field of molecular modelling. Other appendices contain information on
chemical syntheses or other information that is not included in the text for readability
reasons. Computational routines, input and output files from simulations will be made
available from author in electronic form.
2 Introduction

Following the historical course of development of separation equipment and devices, this chapter introduces phenomenologically three issues from the point of view of process intensification and device miniaturisation. It begins with a short introduction to solvent and chemoselector based absorption and continues with its comparison to membrane contactors and further to liquid membranes. Next, basic separation principles in liquid membranes with and without carriers are discussed. Finally, the focus turns to the literature review of already acquired mass transport models for some selected dense membranes with and without carriers.

2.1 Miniaturizing of Processes

All molecular separation processes are based on differences in at least one physical property of the chemicals to be separated. Looking at two examples, namely at separation of olefines from their mixtures with paraffines (e.g. ethylene/ethane or propylene/propane) and separation of oxygen from air, one will, in industrial practice, basically encounter only distillation as a means of separation on the large scale. The third example is the purification of gas streams by removal of acid gases CO$_2$, H$_2$S and SO$_2$ using (chemical) absorption. These kinds of processes are usually conducted in large columns, where the differences in vapour pressure of the molecules with respect to the liquid mixture play a crucial role. The equipment is rather robust and simple, but the operational costs might, due to the energy consumption for cooling, heating, compressing and solvent recycling, not be negligible. The absorption media are usually recovered by stripping [16], which must also be considered in the costs calculations. Basic principles of distillation as well as absorption processes are well known and are described in basic textbooks on unit operations [69].

The main goal of new, innovative separation approaches is to maximise the differences in the physical properties of the respective species and to improve the mass transfer in apparatuses in order to enhance the selectivity and the capacity of the processes. Under this improvements, collected under the term „process intensification”, one understands process performance enhancement by reducing the working volume of the equipment, by increasing operational yield at the constant equipment volume or by energy and material savings in general.

One possible way in the development of alternatives and in the improvement of established separation techniques (cf. also [70]) is e.g. the use of an extra solvent with adjustable properties (e.g. ionic liquids). Furthermore, this solvent can be equipped with a chemical
substance that selectively interacts and/or reversibly reacts with one component in the input mixture. This compound is then usually called a „carrier“. Yet another way is to use novel types of customised equipment in addition to the novel chemical media.

Proceeding with the example above: whereas in a classical distillation column separation of propylene/propane requires large reflux ratios and large number of theoretical plates, an attractive application of the combination ionic cuprous salt/nonaqueous solvent\(^1\) in an extractive distillation process significantly reduces the energy requirements of the separation [71]. The scheme of this separation is shown in Fig. 2.1a. It is a two stage process, still conducted in a column arrangement of a distillation: a mixture of A (propane) and B (propylene) is introduced to the first column, where B has greater affinity to the (pure) solvent system \(S_0\) than A. In the second column, solvent is recovered and B discharged from \(S_0\) by changing operating conditions, which can, in contrast to classical distillation, be adjusted individually to each column yielding greater separation performance. In almost the same manner, absorption of CO\(_2\) is performed by aqueous solutions of alcoholamines (MEA, DEA, [72, 73]).

![Diagram of separation processes](image)

Figure 2.1: Miniaturisation of the reactive separation processes, where \(S_C\) denotes the solvent system with dissolved carrier.

Commercial-solvent based extraction of oxygen from air is not known. However, pressure swing absorption (PSA) with solid ad- and absorbents (be a fixed-bed of zeolites or a fixed-bed of particles impregnated with special cobalt-complex compounds) for this separation, also conducted in comparable column-like arrangement, represents the state-of-the-art for small, mobile applications [74, 75].

The second arrangement is the liquid membrane contactor (MC), the device that provides high phase contact areas. A MC is usually treated separately from both thermal unit operations and liquid membranes in common textbooks, but here it can be considered to be the next stage in the miniaturisation of reactive extraction processes. Membrane contactors can be used for gas/liquid, vapour/liquid [76] and liquid/liquid reactive separation [77]. However, they have been encountered with scepticism in industrial circles so far, mainly due to the deficient stability. Several different usage schemes have been proposed: single stage MC is used e.g. for degasing of liquids, two stage MC operation mode that is

\(^1\)Cuprammonium acetate process was developed for C4 olefin/paraffin fraction separation during World War II.
2.1. MINIATURIZING OF PROCESSES

referred to in this context, is shown in Fig. 2.1b. As in extractive distillation, in the first stage, a mass transfer (absorption) from a feed into the liquid in the membrane contactor takes place under favorable conditions for this step. The liquid is then transported to the second stage, where the change in electrochemical potential, i.e. in temperature [78], pressure [79], redox potential [80, 81] or even photon flux [82], is accomplished. In the second contactor this potential change causes the desorption of the absorbed component out of the solvent. The receptor phase is often a non-reactive sweep gas, however, vacuum can also be applied. This continuous process resembles very much the above mentioned extractive distillation as well as the discontinuous pressure swing absorption. It consists of two steps: charging and discharging. In classical modelling approach charging and discharging are often taken as being thermodynamically unambiguously defined. However, both processes, in fact, do not operate at local equilibria. It was shown that in membrane contactors [83] - in the same way as in distillation - the separation strongly depends on mass transport kinetics. This is actually well known: exactly for that reason technical equipment is always dimensioned with empirical „security factors”.

Third arrangement are immobilised liquid membranes (ILM), often also called supported liquid membranes (SLM).

The process concept of SLM is even more compact than MC. By virtually combining the two units of the membrane contactor into a single one, solvent volume is reduced to a thin film, i.e. to the membrane. Phenomenologically, this operation is a step back to the single stage operation. Since such membranes are very thin, only isothermal mode of operation is feasible. The control over the process is much more delicate and allows less degrees of freedom when compared to the two stage processes mentioned above, since in the latter the equipment will still successfully work even at poorly adjusted operation conditions. Recall for example that if in the desorption step higher temperature is used then necessary, desorption will still take place in spite of higher operational costs. In single stage process, however, absorption and desorption must take place reasonably fast at the same temperature.

In spite of operational restrictions, the advantage of all SLM processes is in the performance per costs of SLM’s working medium in dependance on its intrinsic capacity for the desired compound. This can be deduced from the simple fact that the membrane is very thin and the total amount of the working medium is small. For instance: if the total capacity or load (in terms of amount of desired compound per amount of working medium) halves then twice the amount of working medium is required. For expensive media on large scale, where tons of material is needed, doubling of the amount of working medium might represent the crucial restriction for such a process being build up. The use of SLM in this respect is much less limited and may be compared to another innovative technology in the field of catalysis (supported ionic liquid phase, SILP) [84].

A careful reader will notice the parallels, i.e. the common underlying principles, in both non-reactive and reactive operational modes of all these processes. These principles will be pointed out in the next section, treating the subject of liquid membranes in more detail.
2.2 Liquid Membranes

Three groups of liquid membranes can be distinguished:

- biological membranes,
- simple liquid membranes and
- carrier liquid membranes.

The latter two groups in the context of this thesis belong to the human-made membranes. Here, I will refer only to supported liquid membranes as they have been encountered in the previous chapter. Furthermore, the applications targeted in this thesis are gas and vapour separations, therefore liquid-liquid extraction processes by the means of SLM will only be mentioned in passing.

It is often claimed that human-made liquid membranes have been the model system for mimicking biological membranes. This is true under the aspect that biological membranes possess partial fluidity, denoted as liquid mosaic membranes [85]. It is also true that in both types of membranes transport occurs via diffusion (passive) and via carrier mediated (active) transport. The next section is a short excursion in the field of biological membranes, where the basic difference between human-made and biological membranes is pointed out.

2.2.1 Biological Membranes

Basically, three concepts (Fig. 2.2) for the active transport can be found in biological systems: uniporter, antiporter and symporter mechanism (for details see [86]). The carriers, which are highly selective enzymes responsible for the membrane transport, are called porins. They are incorporated into the lipid bilayer providing selective passing channels (pores).

![Figure 2.2: Three transport events through a biological membrane](image)

It must be emphasised that in all systems shown in Fig. 2.2, the transport of species does not take place against their electrochemical gradient, which is often claimed. All of
these selective transport systems require energy, either in the form of the proton-motive force, ATP, or some other high-energy compound. This means that the transport is always coupled. Biological membranes have the capability to accumulate solutes inside the cell and hold them there against the concentration gradient because the selective transport is in most cases designed to be directed just in one way only. This is, except for Donnan-dialysis (ion exchange membranes) and simple dialysis not the case in any kind of human-made membranes, where the transport is usually not coupled and where the driving force for the transport can be obviously described by macroscopically observed parameters (one must not necessarily look at the mechanisms on molecular level).

Another important difference is the thickness of the membrane. Whereas biological membranes consist of a lipid bilayer of some 18 nm, the thicknesses of the thinnest human-made membranes are of at least one order of magnitude above this value.

In the very beginning of the liquid membrane development, the aspects of human-made and biological membranes were treated together (cf. review article [87] and references cited therein). Today, biological membranes, which display selectivities and specific fluxes unsurpassed by any human-made membranes, are the domain of biochemistry. However, they may still be considered to represent the „technical” merit in their performance.

### 2.2.2 Simple Liquid Membranes

So far, not too much has been said about the properties of the liquid membrane phase in the supported liquid membranes. If chemically pure phase is applied (e.g. water, common organic solvents, glycerine, silicone oil, ionic liquid etc.) one speaks about simple liquid membranes.

As in all extractive processes, the membrane phase itself must be chosen in such a way that the desired permeant will more likely enter the membrane through the feed boundary interphase when compared to the other components of the treated entering mixture. Apart from the high capacity (solubility) of the liquid phase for the desired species, care must be taken that the species of interest also show higher mobility, i.e. higher diffusion coefficients over other species in the membrane phase. Unfortunately, the latter is rarely the case.

The basic separation principle for the simple liquid membrane is given in Fig. 2.3a.

The control over the process can be performed by the application and adjustment of external variables (e.g. temperature). The total and partial pressures of components on both sides of the membrane represent the driving force for the mass transport. Of particular importance is the control of fluid dynamics, i.e. of the velocity of the entering (feed) and the leaving streams (permeate/retentate) into and out of the membrane module, where the membranes are mounted in. The flow regime influences the driving force, which is a local variable (the problem of concentration polarisation is discussed in [11]), therefore the design\(^2\) of a membrane module is of great importance in technical applications.

Moreover, membrane phase should display

\(^2\)In this thesis non-optimised membrane modules for different membranes were used for the proof-of-principle only.
2. INTRODUCTION

Figure 2.3: Scheme of the separation principle in supported liquid membranes: a) without and b) with carrier

- as low miscibility with both adjacent boundary phases in liquid systems and
- as low vapor pressure in gas and vapour systems

as possible. Due to the continuous loss of the membrane phase in both membrane types, operation is in long term unstable. Several investigations were performed on the topic of liquid membrane stability [88, 89, 90], also focusing on other physical phenomena (surface tension, wetting etc.). In this thesis, a novel class of materials, ionic liquids, that show virtually no vapour pressure and might, therefore, be ideally suited for gas and vapour separations, will be applied and examined by looking at selected problems.

Furthermore, liquid lamellae forming the membrane within the porous support should be as thin as possible, since the flux through the membrane is generally reciprocal, i.e. inversely proportional to the thickness of the dense layer [91]. It is well known that molecular diffusion in liquids is of some orders of magnitude higher than in solids [92, 16, 93, 94]. Although diffusivities have been so far higher in liquid membranes, these membranes are generally thicker than polymer membranes. In total, the permeabilities and thus the fluxes in simple liquid membranes are comparable to those in other dense membranes. In this thesis, novel support materials will be examined in combination with ionic liquids.

2.2.3 Carrier Membranes - Facilitated or Carrier Mediated Transport

In general, simple liquid membranes exploit solely slightly different physical properties, i.e. solubilities and diffusion coefficients of the permeants in the respective membrane phase.

For a performance improvement (i.e. enhancement of selectivity and flux) of liquid membranes, like in the extractive distillation, carriers can be dissolved in the liquid membrane phase. Carriers increase both liquid phase capacity for selected species and selectively
support the mass transport (permeability) through the membrane. In addition to the difference in purely physical properties of the permeants, chemical or molecular „recognition” becomes of importance [95]. The concept of the combination of simple liquid membranes with dissolved carriers is called the facilitated transport or carrier mediated transport in membranes. This approach (SLRM, supported liquid reactive membrane, which is shown in Fig. 2.3b, can be clearly described as reactive separation process [37].

A lot of work has been performed not only on liquid but also on solid carrier membranes, whereas both underlie the same basic principles. For olefin separations, predominantly silver(I) and copper(I) salts have been incorporated in different polymer matrices [96], where polymers have often been functionalised (Nafion) [97, 98, 99, 100, 101]. For the separation of carbon dioxide or other acid gases from e.g. natural gas, organic amines have been in use. Details will not be treated any further in this work and can be found in the selected publications, e.g. [102]. It is important to notice, however, that the „hopping mechanism” (Fig. 2.3), which is usually attributed to solid carrier membranes, also takes place in liquid membranes by isentropic exchange reactions. These cannot be macroscopically observed and the characterisation requires sophisticated (radioactive) tracer techniques for revealing the phenomenon.

The requirements that hold for simple liquid membranes used in gas or vapour separations must be further extended. In addition to nonvolatile liquid constituting the membrane phase, transport enhancement of passive liquid membranes is ideally achieved by using a nonvolatile complexing agent (carrier) [103].

In recent work on supported liquid carrier membranes [104, 105, 106], alternative solvent (glycerine) is used with conventional carriers. Since the broader commercial availability of ionic liquids, several projects of exploratory character with these materials were reported [107, 108, 109, 110].

Finally, I would like to turn to the qualitative comparison of simple liquid membranes without carriers and facilitated transport membranes [111]. Let component A have lower intrinsic affinity to the membrane material than the component B. The flux through the membrane depends on the driving force, which is symbolically denoted by transmembrane difference of electrochemical potential at the membrane surface in the Fig. 2.4. In case of a simple membrane, the dependance is linearly proportional, the proportional factor being the diffusion coefficient. The typical enhancement of the solute’s (B) flux over simple solution-diffusion membrane by usage of carrier is represented in Fig. 2.4b. It is important to realise that the presence of the carrier in the liquid phase of the membrane at technically reasonable concentrations (approx. 1 mol/kg) does not significantly change the intrinsic properties of the liquid and that transport via simple diffusion will take place almost independently and in parallel to the carrier mediated transport. Thus, the total flux of B is given by addition of diffusion and facilitated fluxes.

Also very important is that the selectivity reaches its maximum value at infinite dilution in the feed side, i.e. when no chemical potential difference is applied on the membrane. However, considering technically reasonable fluxes at sufficiently high selectivities are achieved when free carrier sites are still present in the mixture [91]. Favourable effect of the facilitated transport on the selectivity thus decreases with increasing saturation. In
this sense, the total amount (concentration) of the carrier in the membrane phase does play a crucial role in the membrane’s performance enhancement.

In the next section, important parameters for understanding the mass transport through the liquid membranes will be pointed out. Furthermore, a few data acquisition methods for these parameters used later in this thesis will be introduced here. Finally, control options over the permeation process will be presented.

### 2.3 Quantities that Determine the Behavior of SLM

According to the solution-diffusion model, the ability of a simple dense liquid membrane to control the permeation of different species is based on the differences in their solubilities and diffusion coefficients in the membrane phase [112]. Both, the diffusion coefficient and the solubility depend on the properties of the particular molecular environment and on the system’s temperature and pressure.

Solubility is usually determined experimentally [113]. However, today it can also be estimated by application of purely computational methods. In this case, the geometry of a given molecule is firstly calculated by quantum mechanical methods, e.g. with density functional theory. Subsequently, continuum solvation model is applied that describes the interaction of molecular environment with the respective molecule. Finally, statistical thermodynamics calculation is performed, which in turn correlates pairwise molecular interactions of molecular ensemble to e.g. Henry’s coefficient (cf. Appendix B and [114]).

The mobility of the molecule within the membrane phase depends mostly on the size of the molecule as well as on the viscosity of the (liquid) membrane phase. Viscosity can easily be measured as parameter. Reliable measurements of diffusion coefficients are, on the other hand, very difficult to perform [115]. Apart from the experimental methods (e.g. Taylor dispersion), two more approaches for obtaining temperature dependant data on diffusion coefficients are possible. One can apply either molecular dynamics (MD) simulation or
2.3. QUANTITIES THAT DETERMINE THE BEHAVIOR OF SLM

existing empirical relationships [116]. MD simulations are quite time consuming [117] and generally do not yield better results than engineering empirical relationships.

We should keep in mind that the higher the temperature, the lower is the solubility of gases and vapours at given partial pressures\(^3\). At the same time, diffusion coefficients significantly increase with rising temperature.

How is the situation in the case of carrier membranes? As stated above, one can use so called carrier as a solute in the liquid phase of the membrane in order to enhance the solubility of the desired component. In this case, the apparent solubility of the respective component will be enhanced, because new species (i.e. modified desired component) in the membrane are formed. As a consequence, the concentration of the non-modified component solute decreases and more of it can be dissolved in the membrane phase following simple solubility rules. The higher the (total) concentration of the permeant in the liquid membrane, the higher the flux through the membrane. Consequently, the concentration of the carrier in the membrane phase should be also as high as possible.

Heuristic rules have been found [103], which state that the reversible carrier reaction with the desired permeant must in every case be spontaneous at the feed membrane side at the given experimental or operating conditions. The carrier reaction can therefore in principle be either exothermic or endothermic, when the entropy term contributes to the overall exergonic behavior, \(\Delta_r G < 0\):

\[
\Delta_r G = \Delta_r H - T\Delta_r S
\]

Since the entropy will always decrease in case of the permeant addition to the carrier, \(\Delta_r S < 0\) (2 molecules join to form one molecule, thus reducing the number of involved particles, therefore causing higher „order” of the system), the endothermic reactions, where \(\Delta_r H > 0\), rule out completely.

Now, we have strong temperature dependance of the solubility, of the viscosity (diffusion coefficient) and of equilibrium constant for the carrier reaction (which now also determines the overall solubility). In the liquid phase (and not at the phase boundary) it also holds:

\[
\Delta_r G = -RT \ln K_a,
\]

where \(K_a\) is the thermodynamic equilibrium constant for the permeant-carrier reaction. This constant can be either directly measured or indirectly determined by the help of the thermochemical tables or calculated through quantum chemical methods. It is important to notice, that the transformation of the concentration related equilibrium constant \(K_c\) to thermodynamic one can be easily performed, when physical properties of the mixture are known. For ideal gas systems the conversion is easy, for liquid mixture the knowledge of density and/or partial molar volumes is necessary. In liquid systems, one also has to operate with concentration dependant activity coefficients, which leads to really

\(^3\)It was observed for oxygen in water and also for hydrogen in different organic liquids that at elevated temperatures sudden increase in solubility occurs. However, thereby pressures of more than 50 bars are required. For the pressure and temperature ranges within which the considerations and experiments are performed in this thesis, these facts are irrelevant.
complicated treatment of reaction thermodynamics. Furthermore, direct pressure effects on equilibrium in liquid phase can usually be neglected.

In case of available reaction enthalpy, which can be assumed to be constant over a broad range of temperatures, van’t Hoff equation can be taken in consideration [118]:

\[
\frac{\partial \ln K_a}{\partial T} = \frac{\Delta_r H}{RT^2}
\]

Since the liquid membranes are very thin, isothermal conditions for the process can be assumed. Overall steady-state reaction within the membrane phase is isenthalpic: it is exothermic on the feed side and endothermic reaction on the permeate side (reversed reaction is forced by continuous mass transport from the permeate membrane surface).

Thus, carriers used in liquid carrier membranes undergo spontaneous exothermic reversible reaction. In order to increase the conversion in this type of reactions, one has to decrease the temperature. Decreasing the temperature causes an increase in viscosity and decrease of diffusion coefficients. This holds equally for liquid and polymer carrier membranes. Because of the delicate balance between all the temperature dependant physical quantities, optimum operation conditions for which the selectivity and the permeability is maximized in a liquid carrier membrane separation, lie in a much narrower window than e.g. for the extractive distillation or for the membrane contactors, where the same quantities can be controlled for absorption and desorption independently and separately from each other. More information is available in [35, 96, 103, 111, 119].

Whereas in the simple solution-diffusion membranes (as well as e.g. in the distillation) exclusive thermodynamical treatment is more common, in membranes with and without carriers or in membrane reactor arrangement kinetics approach is needed, which also seems more reasonable. The reaction kinetics is given by power low equation and the temperature dependance of reaction rate constants \( k_{\text{forwards}} \) and \( k_{\text{backwards}} \) by Arrhenius relationship - no better approach has been found so far for engineering purposes. In very strict treatment, reaction thermodynamics (thermodynamic equilibrium constant \( K_a \), reaction enthalpy \( \Delta_r H \)) must also be considered, because the operation can no longer be considered isothermal. Consequently, more data (e.g. heat capacity and heat conductivity data) are needed. In the following section, short literature review on mass transport modelling in dense membranes is performed.

### 2.4 Existing mass transport models and remarks

There exist only a few papers - if any at all - that deal with the modelling of liquid carrier membranes with respect to the theory of multicomponent transport. Almost no effort has been undertaken so far to model liquid carrier membrane together with the feed and permeate sides from the best of the authors knowledge.

One of the first reviews referring to the mathematical treatment of the membrane transport based on the thermodynamic considerations was made in the late 70-ies [120]. Simple and facilitated membranes are treated, with special focus on biological membranes (ATP and Na\(^+\) transport). Firstly, reverse osmosis membranes are targeted as the simplest case
for the modelling. Next, facilitated membranes are considered [121]. Finally, complex membranes like those applied in the electrodialysis are discussed. On these considerations, nowadays routinely applied solution-diffusion model was developed [122, 112, 32], which was sufficiently explained above.

Thorough mathematical treatment for one-dimensional carrier mediated diffusion in membranes was also performed [87]. This work includes the approximate solutions for cases involving multiple permeant and carrier species that undergo one or more chemical reactions. Interestingly, crude boundary layer analysis is also performed. Recently [123], this analysis approach was used for the consideration of the whole feed and permeate compartments.

Facilitated transport of carbon monoxide through cuprous chloride solutions was both experimentally investigated and modelled theoretically [124]. The reference is useful in three respects. It provides another review of the work in the field, describes the new investigation concept (radioactive tracer technique) and considers the kinetics modelling approach.

Steady state modelling approach based on an empirically defined Langmuir-ansatz for the absorption and desorption equilibria on the phase boundaries was used for facilitated transport of oxygen through liquid membranes [125]. Investigated carriers belong to cobalt-salen family. The Langmuir-ansatz correlates the saturation of the liquid with the oxygen partial pressure according to the carrier-oxygen equilibrium constant ($K_c$). This model is a deviation of the classical solution-diffusion model and is in its nature not defined according to exact thermodynamics.

A reactive diffusion model was used in describing carbon dioxide permeation through an amine functionalised carrier membrane [126]. References cited within the paper are important for classical understanding of modelling of phase boundaries.

For liquid membranes it is often assumed that free and loaded carrier moves through the membrane phase only by diffusion. However, the „hopping” model, known from fixed site carrier membranes, where active groups display limited mobility, cannot be excluded in the mechanistical considerations, since both mechanisms may take place simultaneously. In the theoretical work on facilitated diffusion [128], it could be shown that facilitated transport may only take place above a critical concentration of the carrier sites, where active sites are close enough to each other. There, the percolation threshold is small enough for handing the desired permeant over to the next active site. In this treatment, fast reactions on the membrane surface are assumed, leading to the direct application of the Thiele modulus in the mass transfer equation.

However, in the later general treatment of the fixed site membranes [129], where series of mass transfer resistance model is used, it was demonstrated that facilitation will occur even when the active sites are actually too far apart for direct solute hopping.

Recently, a purely analytical solution for the transport inside a carrier facilitated transport liquid membrane was developed [130]. The model is limited to one dimensional transport.

---

4Please note, that in no way hopping should be considered to be tunnelling. This term is reserved for quantum mechanics and describes a highly improbable event for a reaction concerning very small molecules (e.g. proton transfer) [127].
across the membrane and uses fixed diffusion coefficients and fixed concentrations at phase boundaries.

Most of the above described models assume fixed chemical potentials, i.e. concentrations at the bulk phase boundaries on the feed and on the permeate side of the membrane. Actually, thereby only the membrane phase is considered. It should be noted that the results from the basic solution-diffusion model (at steady state conditions) must in principle be obtained by applying any kind of more complex model that holds either for carrier or for reactive membranes. In the former case, one has to reduce the carrier concentration to zero, in the latter case one has to reduce the carrier/catalyst reaction rate to zero.

Further modelling examples of liquid-liquid membrane systems can be found in the literature, e.g. in [131, 132, 133, 134, 135].

2.5 Summary of Thesis’ Context and of Introduction

The subject of this thesis are dense liquid membranes. Simple liquid membranes consist of the pure liquid membrane phase and work on the principles of the solvent based extraction. Performance enhancement can be achieved by dissolving of carriers into the liquid phase. Carriers can be considered to be catalysts, since they are involved in the reaction and accelerate the process but are themselves not consumed during the process. Therefore, liquid carrier membranes belong to catalytical membranes. Carriers reversibly react with one desired component of the mixture. Careful choice of the solvent, of the support that determines the stability and thickness of the liquid membrane, of the carrier and of the operation conditions is necessary in order to find optimum conditions for a separation with liquid carrier membranes.

In the next chapter, a general mass transport model will be developed, that can, in principle, be applied to any dense membrane system, independent of the species and the materials involved. Modelling should provide an answer to the most important question: Which carrier among the potential chemical compounds can be used under technically reasonable and feasible conditions?
3 Mass Transport Modelling

In this chapter mass transport modelling through a liquid carrier membrane will be dealt with. Drawing up a mass transport model that includes all relationships qualitatively mentioned in the previous chapters seems to be essential for the proper understanding of this kind of reactive separation, which in turn also appears to be decisive for the development and the optimisation of this interesting separation process.

I will confine the treatment of the problem to the two models in this context. The first of them, one dimensional one, was already published [130]. It provides an analytical mathematical solution for the problem of the transport of the active component through the liquid carrier membrane. It describes only the membrane active layer without the adjacent phases. Here, this model is used directly from the literature by simply plugging in the appropriate input variables, i.e. „boundary conditions” for a particular case. It is included in this work for the comparison with the second, integral one, where a membrane module as a whole is considered and which is set up in three dimensions using finite elements method by Femlab software. Although the particular cases that these two modes cover are chemically not the same, in terms of thermodynamic considerations the results from the latter model reasonably supplement and extent the results from the former, simpler one. For the background of the first model one should refer to the original publication. The development and the setup of the second model will be presented in more detail.

We are particularly interested in the desired thermodynamic properties of a chemoselector dissolved in the membrane that enhances both the selectivity and the flux through the membrane. Therefore, the equilibrium constant of a carrier reaction must be implemented into the model as a parameter. In the simulations, this parameter will be varied at discrete values in order to determine the optimum equilibrium constant, at which the selectivity of the liquid membrane separation is maximised. From the equilibrium constant the Gibbs free energy for the carrier reaction can be determined. For better understanding of the thermodynamical relationships, I will give a short note on the proper treatment of chemical equilibrium in the final part of the chapter.

3.1 Introductory definitions

Figure 2.4 from the previous chapter qualitatively shows the effect of carrier-mediated transport on the total flux through the membrane. The diffusion transport through the membrane depends proportionally on the concentration difference of the transported species i on the both sides of membrane, while the carrier-mediated transport converges towards a maximum value, which is dependant on the concentration of the carrier in the
membrane. Both transport processes take place at the same time and add up to a total mass transfer through the liquid membrane. However, in this picture a working carrier system at particular constant temperature is assumed. The temperature is the crucial variable in the carrier mediated membrane transport: it influences the solubility of gases and vapours in the membrane, their diffusion coefficients and the equilibrium constant of the reaction between a carrier and an active component. Before we turn to the models themselves, we have to define some quantities needed for the evaluation of the separation.

Facilitated transport is quantitatively characterized by the so called enhancement factor $\chi$, which is defined as the ratio of the actual solute flux of component $i$ (with chemical reaction) to the solute diffusion flux of component $i$ (without chemical reaction):

$$\chi = \frac{J''_{i,\text{with carrier}}}{J''_{i,\text{without carrier}}}.$$ 

Another characteristic parameter describing the performance of facilitated transport is the facilitation factor $\phi$ which is given by

$$\phi = \frac{J''_{i,\text{with carrier}} - J''_{i,\text{without carrier}}}{J''_{i,\text{without carrier}}} = \chi - 1.$$

In both above definitions it is referred to reactive component only. For the complete evaluation of the process performance, which also includes the selectivity, we also have to include the inert component into the considerations. In general, the selectivity for binary mixtures is defined as the ratio of the permeate and of the feed side molar fractions of the two considered components [11]:

$$S_x = \frac{x_{i,\text{reactive}}}{x_{i,\text{inert}}} \cdot \frac{x_{j,\text{inert}}}{x_{j,\text{reactive}}}.$$ 

This definition is used in the complex model in this thesis, where true mixtures are dealt with. However, other definitions of selectivity are also possible and in case of evaluation of permeation of pure components even unavoidable. In the simple model as well as in the initial measurements described in experimental chapter only individual fluxes through the membrane are determined. In order to still assess the performance of the membrane process, the selectivity is either quantified by the ratio of the flux of the one (reactive) component $i$ to the total transmembrane flux $(i+j)$ or simply by the ratio of the fluxes of both pure components:

$$S_r = \frac{J''_{i,\text{reactive}}}{J''_{\text{total}}} = \frac{J''_{i,\text{reactive}}}{J''_{i,\text{reactive}} + J''_{j,\text{inert}}}; \quad S'_r = \frac{J''_{i,\text{reactive}}}{J''_{j,\text{inert}}}.$$ 

The latter selectivity definition is known under the term permselectivity.
3.2 Simple Model

As mentioned above, Al-Marzouqi presents an analytical expression for the facilitation factor of the reactive component A that permeates through a liquid membrane in his paper [130]. According to the reaction equation $A_{(g)} + B_{(l)} \rightleftharpoons AB_{(l)}$, A reacts in an instantaneous and reversible complexation reaction inside the liquid membrane with a component B, which represents the carrier, to a complex AB (adduct). The analytical solution for the facilitation factor considers unequal diffusion coefficients for the solute A, for the carrier B, and for the complex AB. It must, however, be noted that only mass transfer within the membrane is considered. In particular, any mass transfer to and from the interfaces is neglected in this model. Since no mass transport resistances at phase boundaries (feed-membrane and permeate-membrane) are included into considerations, the boundary conditions are not subject to change. This means that at the phase boundaries fixed concentrations are assumed. Furthermore, these concentrations are considered to be not dependant on the temperature\(^1\).

3.2.1 Facilitation Factor and Permeate Flux

It was shown that the facilitation factor $\phi$ can be calculated according to the equation:

$$\phi = \frac{\alpha K_c c^*}{D_A (1 + (\alpha K_c c_{A0}) (1 + (\alpha K_c c_{AL}))},$$

where $\alpha$ is the ratio of the diffusion coefficients $D_{AB}$ and $D_B$, $K_c$ is the concentration dependant equilibrium constant of the permeant-carrier reaction, and $c_{A0}$ and $c_{AL}$ are the concentrations of A at the feed interface ($x=0$) and the permeate interface ($x=L$) of the membrane, respectively. $D_A$ is the diffusion coefficient of the pure permeant and the variable $C^*$ a complex function of all these known variables. It is eliminated during the evaluation procedure.

The flux of the solute A through the membrane can be finally derived from the equation

$$J'_A = (1 + \phi) \frac{D_A}{L} (c_{A0} - c_{AL}),$$

which in its form strictly corresponds to the first Fick’s Law. The equation form for the inert component corresponds to the form for the solute A, but does not include the facilitation factor ($\phi=0$).

3.2.2 Case study details and results

The above equations are used to calculate the facilitation factor and the flux through a supported liquid membrane, which are the primary target quantities. The main question

\(^1\)Concentration in the membrane phase depends on the gas solubility in the membrane liquid. Solubility at 293.15 K was taken - cf. Table 3.2
to be answered is however, what is the optimum equilibrium constant $K_c$ for the maximum performance of the membrane separation. In order to determine the optimum equilibrium constant, more or less realistic temperature dependant data based on the chosen materials are taken. In the model equation the systematic variation of the equilibrium constant $K_c$ for discrete values is performed.

The liquid membrane is made of ionic liquid [BMIM]$^+$ [BTA]$^-$, which is immobilised in a porous structure. This support is not further considered in the simple model. The feed stream of the separation process consists of a 50:50 mixture of propylene and propane at 3 bar total pressure. On the permeate side, fixed partial pressures of 50 mbar for each component are assumed, which are maintained by a vacuum pump. The deviation from the 50:50 ratio in the permeate phase due to different permeation rates of propane and propylene through the membrane are neglected. As an exemplary carrier the compound Ni-dithiete$^2$ is considered. It is assumed that the carrier is homogeneously distributed throughout the membrane.

The acquisition of the required variables and parameters specified in the above equations is adopted from the literature [116] and some parts of the calculations are presented in the Appendix A. The solubilities of the propylene and propane in the liquid phase were determined experimentally (measurements are described in Chapter 5). Before presenting the solution of the simple case study, these parameters are summed up here first.

Diffusion Coefficients

In Table 3.1 the diffusion coefficients at infinite dilution of propylene, propane, carrier, Ni-dithiete, and the carrier-permeant complex in a temperature range between 275 K and 425 K are presented, which were used in this study. These temperatures are considered to be reasonable operating conditions of the liquid membrane in the case study.

<table>
<thead>
<tr>
<th>Temp [K]</th>
<th>$D_{\text{Propane}}^0$</th>
<th>$D_{\text{Propene}}^0$</th>
<th>$D_{\text{Ni-dithiete}}^0$</th>
<th>$D_{\text{Ni-complex}}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>275</td>
<td>$2.43 \times 10^{-03}$</td>
<td>$2.60 \times 10^{-03}$</td>
<td>$9.88 \times 10^{-10}$</td>
<td>$8.79 \times 10^{-10}$</td>
</tr>
<tr>
<td>293.15</td>
<td>$7.10 \times 10^{-09}$</td>
<td>$7.59 \times 10^{-09}$</td>
<td>$2.89 \times 10^{-09}$</td>
<td>$2.57 \times 10^{-09}$</td>
</tr>
<tr>
<td>325</td>
<td>$2.89 \times 10^{-08}$</td>
<td>$3.09 \times 10^{-08}$</td>
<td>$1.17 \times 10^{-08}$</td>
<td>$1.04 \times 10^{-08}$</td>
</tr>
<tr>
<td>350</td>
<td>$6.75 \times 10^{-08}$</td>
<td>$7.22 \times 10^{-08}$</td>
<td>$2.75 \times 10^{-08}$</td>
<td>$2.44 \times 10^{-08}$</td>
</tr>
<tr>
<td>375</td>
<td>$1.38 \times 10^{-07}$</td>
<td>$1.47 \times 10^{-07}$</td>
<td>$5.60 \times 10^{-08}$</td>
<td>$4.98 \times 10^{-08}$</td>
</tr>
<tr>
<td>400</td>
<td>$2.54 \times 10^{-07}$</td>
<td>$2.72 \times 10^{-07}$</td>
<td>$1.03 \times 10^{-07}$</td>
<td>$9.20 \times 10^{-08}$</td>
</tr>
<tr>
<td>425</td>
<td>$4.36 \times 10^{-07}$</td>
<td>$4.66 \times 10^{-07}$</td>
<td>$1.77 \times 10^{-07}$</td>
<td>$1.58 \times 10^{-07}$</td>
</tr>
</tbody>
</table>

When comparing the data in Table 3.1, one can observe that within the chosen temperature range the diffusion coefficients cover three orders of magnitude. Due to the increased

$^2$bis-cis-(1,2-perfluoromethylene-1,2-dithiolato)nickel
molecular motion of the system, diffusion is increased at higher temperatures. Compared to propylene or propane, diffusion coefficients of Ni-dithiete and the Ni-complex are smaller, which can be explained by the size of the molecules. Diffusion coefficients of propylene and propane do not differ significantly from each other.

**Solutes’ Concentrations at the Membrane Interfaces**

The knowledge of the concentrations at the phase boundaries are required for the calculation of the facilitation factor, of the flux through the membrane and of the selectivity according to Al-Marzoqui equations. Hereby, we must distinguish between the feed side and the permeate side due to different pressure conditions. In both models I present here, vapor-liquid equilibrium (VLE) is assumed at the interface between the vapor and the liquid phase, i.e. the membrane phase solution at the interfaces is saturated by the vapour at given conditions.

The solubilities of gases or vapours in any liquid depend on the temperature, on the partial pressure of the gas/vapour over the liquid, on the nature of the solvent and on the nature of the gas. VLE are often determined by using certain models such as NRTL, UNIQUAC and UNIFAC or the even somewhat more limited Soave-Redlich-Kwong model. These models are very powerful, since they describe non-ideal behavior of fluid mixtures. However, they require binary parameters, which cannot be predicted and must be derived from experimental data.

For the calculation of gas solubilities Henry’s Law is used, where the Henry’s constants are acquired experimentally. I do not use the thermodynamically correct equation, where pressure is correlated to the mol fraction of the gas/vapour in the liquid. Instead, since liquid concentrations in mol/m$^3$ are required in the simple model, the vapour pressure is related to the concentration of the species $i$ according to:

$$p_i = H_i c_i$$

The gas solubility, i.e. the concentration $c_i$ of gas $i$ in the liquid is directly proportional to the partial pressure $p_i$ of the gas over the liquid. Henry’s Law is assumed to be valid only at low pressure conditions. In our case the partial pressure does not exceed 1500 mbar, hence the method can be applied$^3$. On the permeate side, total pressure of 100 mbar is assumed, which again is split in equal contributions for propylene and propane. The data applied here is presented in the Fig. 5.10.

The concentrations of propylene and propane at the interfaces of the liquid membrane are presented in Table 3.2.

The concentration of propane does not appear in the model of Al-Marzouqi, but is required later when calculating the selectivity of the membrane process. The calculation is analogous to propylene.

Finally, since the concentration of the carrier in the membrane phase crucially influences the separation performance of the membrane unit operation it must be known. For aque-

$^3$The mechanical stability of the membrane was found to be limited by (total transmembrane) pressure of 3 bar. Applying a 1:1 feed mixture of propane:propylene yields 1500 mbar of each component.
Table 3.2: Concentration of propene at interfaces of liquid membrane at 293,15 K

<table>
<thead>
<tr>
<th>Interface</th>
<th>Pressure [mbar]</th>
<th>Concentration [mol/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{\text{propene,0}}$ feed phase</td>
<td>1500</td>
<td>201.61</td>
</tr>
<tr>
<td>$c_{\text{propene,L}}$ permeate phase</td>
<td>50</td>
<td>6.72</td>
</tr>
<tr>
<td>$c_{\text{propane,0}}$ feed phase</td>
<td>1500</td>
<td>113.04</td>
</tr>
<tr>
<td>$c_{\text{propane,L}}$ permeate phase</td>
<td>50</td>
<td>3.77</td>
</tr>
</tbody>
</table>

ous liquid membranes/membrane contactors [78] it was found that carrier concentrations of around 1 mol/l (1000 mol/m³) can be realised. Although such high concentrations of carriers still have to be achieved in ionic liquids (cf. experimental chapter), I will use this concentration in the modelling part. Thus, this value must be thought of as the benchmark.

Results

Facilitation factor, fluxes, and the selectivity can now be calculated for the particular conditions stated above.

Facilitation Factor: Figure 3.1 shows the effect of the equilibrium constant $K_c$ on the facilitation factor of propylene for the case study using simple model.

![Facilitation Factor](image)

Figure 3.1: Dependance of the facilitation factor for propylene transport through the membrane on equilibrium constant

It can be observed that at very low equilibrium constants, where almost no reaction, i.e. no conversion takes place, the facilitation factor logically have the value of zero. Then it increases to a maximum value, and finally as the value of the equilibrium constant is increased, i.e. when all carrier molecules are completely converted to the adduct, it drops back to zero. In our case study it reaches the maximum value at around $K_c = 0.03$ m³/mol and accounts for $\phi = 1.18$. Under these conditions the flux of the active component
propylene, which is based on carrier-mediated transport, is up to 1.18 times higher than its pure diffusion flux.

**Flux:** For the calculation of the flux through the membrane one also has to assume the thickness of the membrane’s active layer. Since a selected liquid membrane support used in the experiments (Whatman support, cf. Chapter 5) displays a thickness of 60 µm and this support is fully wetted with the liquid, this value was taken in this case study. The results are presented in Fig. 3.2.

![Figure 3.2: Total flux of a) propylene and b) propane at different equilibrium constants and temperatures](image)

**Selectivity:** In Fig. 3.3 the results for both definitions of selectivity are presented. In the first definition the selectivity of 1 means that only one component permeates. We have obtained 80%. The ratio of the individual fluxes seems to be more straightforward for the evaluation of the performance in respect to the selectivity: propylene permeates 4 times faster through the membrane than propane.

![Figure 3.3: Flux based selectivity for propylene/propane separation vs. equilibrium constant](image)

The data is not temperature dependant, since the diffusion coefficients underly the same correlation and do not change relative to each other. Additionally, one of the reasons for
this behavior is also that the concentrations at the both membrane boundaries are taken
to be fixed.

3.3 Complex Model

In contrast to the simple model, where only the membrane phase is modelled, this section
presents the treatment of the completely assembled membrane separation unit, which
is also used in experimental work. In order to recall the real experimental situation, I
will first shortly introduce the setup and describe the carrier reaction and the operating
conditions. Modelling approach will be treated in more detail next. Finally I will turn
to the results obtained by performed simulations. It has to be noted again that the
focus of the study is aimed at the determination of optimum equilibrium constant of the
carrier-desired permeant reaction for the separation.

3.3.1 Membrane Module: Geometry, Carrier Reaction, Operating Conditions

A general scheme of the membrane unit separation unit is shown in Fig. 3.4a.

![Diagram of membrane module](image)

Figure 3.4: Membrane unit: a) general flow-sheet b) geometry details of the membrane
module (the sketch of velocity profile was adopted from literature [136])

The feed, a mixture of propane and propylene enters the membrane module, where the
part of it, preferably propylene is (reactively) absorbed in the liquid membrane and diffuses
through the membrane. At the permeate side the diffused fraction is diluted by the sweep
gas (pure nitrogen) and exits the module. The dilution of the diffusing species in nitrogen
leads to a lower partial pressure of the diffusing species on the permeate side resulting
in higher driving force for the diffusion process across the membrane. The sweep gas is
introduced into the module co-current to the feed flow.

Geometry: The cut through the membrane module is shown in Fig. 3.4b. The module is
of cylindrical shape, feed and permeate sides are divided by a porous ceramic structure,
which acts as a support for the ionic liquid. Although permeate and feed side can be flipped, in theoretical and experimental part of this work, the inner compartment is treated as the feed side. The membrane module measure 224 mm in length, with an outer diameter of 20 mm and wall thickness of approximately 1 mm. The feed compartment diameter, which is actually the inside of the porous ceramic membrane support, measures 1.9 mm and the has an overall thickness of 0.5 mm. The ceramic layer consists mainly of aluminum oxide (Al₂O₃) with the mean pore size of 3 nm. At the feed membrane phase boundary is the active membrane layer made of titanium dioxide (TiO₂) with a mean pore diameter of 0.9 nm and a thickness of 10 µm. Exact porosity of the ceramic is unknown - an estimated value by the manufacturer (HITK, Hermsdorfer Institut für Technische Keramik, Hermsdorf, Germany)) is 0.25.

The liquid membrane layer is created by wetting the inner surface of the ceramic structure with ionic liquid. The liquid is held in the pores by capillary forces. Again, the ionic liquid [BMIM][BTA] is used as the liquid membrane phase. The liquid membrane thickness was estimated to 0.284 mm by weighing the soaked-in liquid and accounting for the support’s porosity. The exact thickness of the ionic liquid layer is, however, unknown. Here it is assumed to be between 100 and 300 µm.

Carrier Reaction: In this treatment, the carrier that reversibly forms a complex with the feed component propylene, is copper(I) tetrachloroaluminate, CuAlCl₄. For this carrier it is assumed that it can be dissolved in the ionic liquid membrane phase up to an amount of one mol per liter of ionic liquid. No activation energy must be overcome for this particular carrier-permeant reaction (cf. Chapter 4). Therefore, an instantaneous equilibrium reaction with unknown, but fast kinetics is assumed. Due to the assumption of fast reaction, kinetics must be then governed by diffusion. Hence, the reaction is sufficiently described by equilibrium constant. The fact that the process may be supposed to be completely controlled by thermodynamics has an important consequence: when the membrane separation process is considered to be in the steady state, and when assuming that the membrane layer is thin enough, the heat formation by the exothermic reaction on the feed side is compensated by the heat consumption on the permeate side. Nevertheless, to ensure isothermal conditions inside the membrane module, the module is appropriately heated and insulated in experiments.

Operating Conditions: In experiments, the feed gas stream consists of 1:1 mixture of propane and propylene, but its composition can also be varied. In total 4 ml of feed are sent into the membrane module per minute. Furthermore, 10 ml/min of sweep gas are introduced into the permeate compartment. The sweep gas is pure nitrogen, which is almost insoluble in the ionic liquid. The total feed side pressure is set to 2.5 bars, that on the permeate side to 1 bar. Inside the membrane module, isothermal conditions can be found due to its insulation. The temperature can be varied and controlled. The temperature range of interest ranges from 0°C and 100°C. For modelling purposes, flow conditions inside the membrane module are of essential importance. A Reynolds number calculations suggest laminar feed and permeate flow in the respective range of temperatures.
3.3.2 Modelling

The modelling of complex processes must be pursued in a systematic manner. Such approach improves the understanding of the model and the modelling process. Furthermore, it enables the existing model to be refined and adopted to related problems more easily. The modelling process can be generally divided in six steps. The aim of the modelling is stated first (1), then the general model structure is defined (2). Next, the system that is to be modelled is decomposed into several elementary components (3), which are each mathematically modelled in detail (4). The model components are thereafter assembled to the complete model (5). Detailed experiment description is necessary in order to analyze and validate the derived model by simulation (6). All the steps of the modelling process can be redefined if the prediction of experimental data proves to be not satisfactory. It should be noted, however, that modelling in general can be approached with arbitrary complexity without gaining accuracy or predictiveness of the model.

Aim of the Modelling

In this work, the model should be able to predict general trends in the unit separation. It is not the aim to predict or reproduce experimental data but rather to describe the stationary behavior of the membrane reactor qualitatively and to some extent also quantitatively using supporting information from experiments\(^4\). The model of the membrane separation unit is intended to be derived under consideration of simplified fluid dynamics for the feed/retentate and permeate phases and with as simple diffusion description in the membrane liquid and in both adjacent phases as possible. Some of the input parameters were stated in previous section, but the assessment methods used here are different. They will also be described here. The equilibrium constant, for which we seek the maximum value, will be varied in the model equations in discrete intervals in order to observe its effects on the process performance. From this data, optimum equilibrium constant value can be derived.

General Model Structure

A model that takes into account the module as one single unit will not be able to fulfill the defined goal of the modelling. The complexity of the given problem demands a decomposition of the complete system, i.e. membrane module into smaller units, which can be modelled in detail. The model and its subunit structure is shown in Figure 3.5, where the model structure is represented by two different kinds of elements: the components are indicated by quadrangles and connections by ellipse-like objects. These elements are called general phases and phase connections, respectively.

The first system-disassembling step is achieved by the separation of the membrane module from its environment. Environment can be modelled as a boundary conditions to the differential equations that describe the physical state of the streams entering and exiting

\(^4\)Nevertheless, some simulated data will be compared to that obtained in the experiments, where applicable.
3.3. COMPLEX MODEL

Figure 3.5: The structure of the complex model

the membrane module. The module itself is further divided into feed and permeate phase and into the liquid membrane. Membrane, which contains the carrier compound for propylene, plays the central role in the model but will not be decomposed into the further components (e.g. active porous layer, support structure, etc.). The components within the module are connected by the phase boundaries between the gas phases and the liquid membrane phase.

**Elementary Model Components** For all individual elements, physical and phenomenological properties are collected prior to the mathematical formulation of the model. This serves to help the modeler to identify all important quantities, which are required for the modelling or are intended to be the result of the model. Furthermore, such documentation helps to improve the reader’s comprehension for the model set-up by making the properties of model’s elements more transparent. For all elements of the model the respective properties are collected in the Table 3.3.

Since the geometry is of cylindrical shape, it is reasonable to set up a 2-dimensional model, choosing cylindric coordinates \((r, z)\) for all three phases. The origin is set to symmetry axis \((r = 0)\) and feed entry \((z = 0)\).

**Mathematical Formulations**

The elementary components of the model are mathematically formulated starting with the feed phase, followed by the membrane and the permeate phase and the respective connections. Every element’s description consists from the necessary equations of change and corresponding boundary conditions, the constitutive equations, from all physical or geometrical constants and input variables.

**Feed Phase - Equations of Change**

For the mathematical description of the phenomena convection and diffusion an equation of continuity for each individual species present in the feed phase, i.e. for propane and propylene must be set. The mass balance in terms of concentration for one single
Table 3.3: Characteristics of the simplified models

<table>
<thead>
<tr>
<th>element</th>
<th>property</th>
<th>description/value</th>
</tr>
</thead>
<tbody>
<tr>
<td>feed phase</td>
<td>species</td>
<td>propane, propylene</td>
</tr>
<tr>
<td></td>
<td>dispersal</td>
<td>homogeneous</td>
</tr>
<tr>
<td></td>
<td>physical state</td>
<td>gaseous</td>
</tr>
<tr>
<td></td>
<td>geometric form</td>
<td>cylinder: outer radius 0.95 mm, length 224 mm</td>
</tr>
<tr>
<td></td>
<td>DE variables</td>
<td>concentrations of propane and propylene</td>
</tr>
<tr>
<td></td>
<td>phenomena</td>
<td>isothermal diffusion and convection (no heat effects)</td>
</tr>
<tr>
<td></td>
<td>streams</td>
<td>entering feed, exiting retentate, diffusive flux</td>
</tr>
<tr>
<td></td>
<td>process variables</td>
<td>through the feed side membrane boundary</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pressure, temperature, diffusion coefficients, etc.</td>
</tr>
<tr>
<td>membrane phase</td>
<td>species</td>
<td>propane, propylene, carrier, complex, ionic liquid</td>
</tr>
<tr>
<td></td>
<td>dispersal</td>
<td>homogeneous</td>
</tr>
<tr>
<td></td>
<td>physical state</td>
<td>liquid</td>
</tr>
<tr>
<td></td>
<td>geometric form</td>
<td>annulus: inner radius 0.95 mm, outer radius depends on the thickness of the support/membrane, length 224 mm</td>
</tr>
<tr>
<td></td>
<td>DE variables</td>
<td>concentrations of propane, propylene, carrier, complex</td>
</tr>
<tr>
<td></td>
<td>phenomena</td>
<td>isothermal diffusion and reaction (no heat effects)</td>
</tr>
<tr>
<td></td>
<td>streams</td>
<td>diffusive flux through the membrane boundaries</td>
</tr>
<tr>
<td></td>
<td>process variables</td>
<td>pressure, temperature, diffusion coefficients, viscosity, solubility, etc.</td>
</tr>
<tr>
<td>permeate phase</td>
<td>species</td>
<td>propane, propylene, nitrogen</td>
</tr>
<tr>
<td></td>
<td>dispersal</td>
<td>homogeneous</td>
</tr>
<tr>
<td></td>
<td>physical state</td>
<td>gaseous</td>
</tr>
<tr>
<td></td>
<td>geometric form</td>
<td>cylinder: inner radius depends on the thickness of the support/membrane, outer radius 9 mm, length 224 mm</td>
</tr>
<tr>
<td></td>
<td>DE variables</td>
<td>concentrations of propane, propylene (and nitrogen)</td>
</tr>
<tr>
<td></td>
<td>phenomena</td>
<td>isothermal diffusion and convection (no heat effects)</td>
</tr>
<tr>
<td></td>
<td>streams</td>
<td>sweep gas inflow, permeate outflow, diffusive flux</td>
</tr>
<tr>
<td></td>
<td>process variables</td>
<td>through the permeate side membrane boundary</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pressure, temperature, diffusion coefficients, etc.</td>
</tr>
</tbody>
</table>
component reads:

\[ \frac{\partial c_i^F}{\partial t} + \nabla \cdot (c_i^F u^F) + \nabla \cdot j_i^F = 0, \]

where \( c \) denotes the concentration of species \( i \) in the feed phase, \( u^F \) the convective velocity vector and \( j_i \) the diffusive velocity of the species. Here, an assumption is made that convection in radial direction can be neglected (i.e. Stefan-correction is not made). This means that only diffusion is responsible for the transport perpendicular to the membrane surface. In addition, the convective velocity inside the feed phase is assumed to be constant for the whole length of the membrane module. This offends the equation of mass continuity for the system, but for small fluxes through the feed-membrane boundary the error should be tolerable. If the mass balance equation above is dimensionally reduced to two dimensional cylindrical coordinates, the equation become:

\[ \frac{\partial c_i^F}{\partial t} + u_F^R \frac{\partial c_i^F}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} (r j_i^F_r) + \frac{\partial}{\partial z} (j_i^F_z) = 0 \]

**Feed Phase - Boundary Conditions**

Prior to the actual formulation of the boundary conditions to the equations of change, all boundaries of the feed, membrane and permeate phase are assigned numbers for the purpose of clarity. In Figure 3.6 the boundaries are numbered from 1 to 10. This notation is used for the whole model. The flow directions of the feed and sweep gas are indicated as well (co-current flow regime).

For the feed phase, the following boundary conditions and assumptions can be derived or postulated:
1. At the axial symmetry axis (boundary 1), all concentration gradients in radial direction of the present species have to be zero.

\[ \frac{\partial c_i}{\partial r} = 0 \]

2. At the feed entry (boundary 2), all concentrations are known.

\[ c_i = x_i^{o,F} c_i^{o,F} \]

3. No diffusive flux \( j_{iz} \) in axial direction. All axial mass transfer is convective.

\[ j_{iz} = 0 \]

This assumption should be feasible, because axial mass transport is, at given flow rates in a real module, dominated by convection.

4. The flux of each component has to be equal at both sides of the feed-membrane phase boundary (boundary 4)

\[ \dot{N}_i^F = \dot{N}_i^M \]

With known boundary conditions for the feed compartment, it is possible to calculate the properties of the flux exiting the module at boundary 3, i.e. retentate.

**Feed Phase - Constitutive Equations**

**Velocity Profile**: Flow conditions are assumed to be laminar in the feed phase. With no convective flux in radial direction, the velocity profile inside the feed compartment can be calculated by a simple momentum balance for Newtonian fluids. The solutions for such balances can be found in [136] and [137]. For flow through a circular tube (feed phase) the following velocity profile \( v(r) \) as a function of the radius \( r \) arises:

\[ v_z^F = v(r) = v_{max}(1 - \frac{r}{R_1})^2 = 2v_{avg}(1 - \frac{r}{R_1})^2. \]

Radial convective velocity is set to zero

\[ v_r^F = 0. \]

\( R_1 \) denotes the outer radius of the feed compartment, \( v_{max} \) is the maximum velocity inside the feed phase, located on the symmetry axis and \( v_{avg} \) is the feed average velocity.

**Diffusion** The feed consists of propane and propylene. Therefore, here it is dealt with a binary diffusion application, which can be described with sufficient accuracy by Fick’s first law:

\[ J_i^F = -D \nabla c_i. \]
3.3. COMPLEX MODEL

Distinguishing between axial and radial vector components leads to

\[ j_{i,r}^F = -D \frac{\partial c_i}{\partial r} \] and \[ j_{i,z}^F = -D \frac{\partial c_i}{\partial z}. \]

For convenience of the implementation, instead of the molar fraction gradient, the molar concentration gradient is used as a driving force. They are equivalent for isothermal conditions [138].

The binary diffusion coefficients were not measured and are not known. Fuller et al. (cf. [116]) provide an estimation method for gases at low pressures, which should be suitable for the modelling of the membrane module operated at 2.5 bars feed pressure. Empiric correlation that yields an average absolute error of approx. 4 % compared to experimental data reads:

\[ D_{ij} = \frac{0.00143 T^{1.75}}{p^F M_{ij}^{\frac{1}{2}} \left[ (\sum_{i}^{\frac{1}{2}}) + (\sum_{j}^{\frac{1}{2}}) \right]^2}. \]

The term \( M_{ij} \) is defined as:

\[ M_{ij} = 2 \left[ \left( \frac{1}{M_i} \right) + \left( \frac{1}{M_j} \right) \right]^{-1}. \]

The correlation determines the binary diffusion coefficient in cm\(^2\)/s of components A and B as a function of temperature \( T \) in Kelvin, the molecular weights \( M_i \) of components A and B in g/mol and the feed pressure \( p^F \) in bar. The terms \( (\sum_{i}) \) are the sums of the atomic diffusion volumes, which are tabulated (C=15.9; H=2.31, N\(_2\)=18.5). For all components in the two gas phases (feed and permeate), the resulting diffusion volumes and diffusion coefficients are listed in Tables 3.4 and 3.5.

Table 3.4: Diffusion volumes for propane, propylene and nitrogen

<table>
<thead>
<tr>
<th>component</th>
<th>diffusion volumes [cm(^3)/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>propane</td>
<td>66.18</td>
</tr>
<tr>
<td>propylene</td>
<td>61.56</td>
</tr>
<tr>
<td>nitrogen</td>
<td>18.5</td>
</tr>
</tbody>
</table>

It can be seen that the binary diffusion coefficients are of same orders of magnitude. Note also that for binary diffusion coefficients holds: \( D_{ij} = D_{ji} \).

Further Equations The following additional definitions have to be given for the treatment of the model:
Table 3.5: Binary diffusion coefficients at 20°C

<table>
<thead>
<tr>
<th>Binary system</th>
<th>Diffusion Coefficient $\frac{cm^2}{s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>feed phase</td>
</tr>
<tr>
<td>propane/propylene</td>
<td>2.80 $\cdot 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>7.00 $\cdot 10^{-2}$</td>
</tr>
<tr>
<td>propane/nitrogen</td>
<td>4.48 $\cdot 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>11.21 $\cdot 10^{-2}$</td>
</tr>
<tr>
<td>propylene/nitrogen</td>
<td>4.66 $\cdot 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>11.64 $\cdot 10^{-2}$</td>
</tr>
</tbody>
</table>

Molar fraction:

$$x_i = \frac{c_i}{c_t} \quad i = 1...n$$

Total feed side concentration:

$$c_t = \sum_i^n c_i ,$$

However, this last formulation does not ensure that the ideal gas law is satisfied. Due to the flux through the feed-membrane boundary the total concentration is not constant in the feed phase. Nevertheless, the error inside the feed phase should be tolerable for small fluxes across the membrane. Hence, ideal gas law determines concentrations at the feed entry as boundary conditions for the mass balance within the feed compartment. The feed total concentration $c_t^{F_o}$ is then given by the ideal gas law

$$c_t^{F_o} = \frac{p^F}{RT} .$$

Average velocity:

$$v_{avg} = \frac{\dot{Q}_t^{F}}{A^F} = \frac{\dot{Q}_{total}^{F}}{\pi R_1^2} ,$$

where $\dot{Q}_{total}^{F}$ is denoted as the feed volume flux and $R_1$ as the feed compartment radius.

**Membrane Phase - Equations of Change**

It is assumed that inside the membrane there is no convective mass transport, i.e. all mass transport occurs by diffusion. This assumption is commonly made in membrane separation calculations (solution-diffusion model). The species inside the liquid membrane are the ionic liquid membrane phase, propane, propylene and the carrier. Under the assumption that the ionic liquid concentration is constant no equation of change for the species ionic liquid is required. The carrier-permeant reaction takes place only within the
membrane phase. It can be characterized in general way by the reaction rate $\dot{r}_i$ of the component $i$.

$$\frac{\partial c_i^M}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (r j_{i,r}^M) + \frac{\partial}{\partial z} (j_{i,z}^M) = \dot{r}_i.$$

**Membrane Phase - Boundary Conditions**

The corresponding boundaries of the membrane phase are shown in Fig. 3.6 and are denoted 4, 5, 6 and 7.

1. The fluxes through the phase boundary 4 must be equal on both sides for propane and propylene, whereas flux of the carrier and its complex is zero across the boundary.

$$\dot{N}_i^M = \dot{N}_i^F \quad \text{for } i = \{\text{propane, propylene}\}$$

$$\dot{N}_i^M = 0 \quad \text{for } i = \{\text{carrier, complex}\}.$$

2. It is assumed that in axial direction there is no mass transport at the boundaries 5 and 6. Hence it holds

$$\dot{N}_i^M = 0.$$

3. Except that the boundary 7 is directed towards permeate compartment, the boundary conditions are identical to those at the boundary 4:

$$\dot{N}_i^M = \dot{N}_i^P \quad \text{for } i = \{\text{propane, propylene}\}$$

$$\dot{N}_i^M = 0 \quad \text{for } i = \{\text{carrier, complex}\}.$$

**Membrane Phase - Constitutive Equations**

**Diffusion** Diffusion coefficients in fluids and particularly in liquid mixtures are, according to the simple model of Stokes-Einstein [16], dependent on the liquid’s viscosity, which is a function of temperature, and on the effective particle radius. Furthermore, if considering diffusion on molecular level, it becomes clear that the composition must also play a crucial role. Although no suitable prediction methods are known with general validity, especially for ionic liquids that are used in this work, for dilute liquid mixtures some correlations have been derived that yield quite reasonable results. One of the best known prediction methods is the application of the correlation of Wilke and Chang [116]:

$$D_{ij} = 7.4 \cdot 10^{-8} \left( \phi_j M_j \right)^{1/2} T \eta_i V_i^{1/6} ,$$

where $D_{ij}$ is the diffusion coefficient in cm$^2$/s of solute $i$ infinitely diluted in solvent $j$, $M_j$ the molecular weight of the solvent in g/mol, the temperature $T$ in K, the viscosity
The molar volume of solute \( i \) at its normal boiling point in \( \text{cm}^3/\text{mol} \) and a dimensionless association factor \( \phi \) of solvent \( j \). The association factor accounts for e.g. hydrogen bonding or electrostatic effects in the solvent.

From an engineering perspective, the calculation of diffusion coefficients at infinitive dilution are often used up to a concentration of \( 5 \) or even \( 10 \) wt.% \[116\]. For multicomponent mixtures some modified equations were also developed (e.g. by Geankoplis et al. cf. \[116\]). Errors that arise using these equations have been reported to be usually within 20 \%, but in certain cases they may be greater - possibly >100\%. The method has not been tested for diffusion in ionic liquids. However, so far, availability of better methods is not known. For the estimation of diffusion coefficients in ionic liquids I use the following equation:

\[
D_{im} = 7.4 \times 10^{-8} \left( \frac{\phi M}{\eta m V_i^0} \right)^{0.5},
\]

where instead of the pure solvent’s properties, its mixture properties are taken into account by summation of molar volume and association factor increments in the ratio of respective mol fractions according to:

\[
\phi M = \sum_{j=1, j \neq i}^{n} x_j \phi_j M_j.
\]

The association factors for all components (propane, propylene, carrier and corresponding complex) are chosen to be one, since it can be assumed that these molecules do not influence each other in the mixture. The exception is the value of 2,2 for ionic liquid, which is charged and may build hydrogen-like bonds.

The molar volumes can be calculated by the use of Le Bas additive volume increments, which are tabulated \[116\] and are available for the most common groups constituting chemical compounds. Where data is missing, as in the case of the carrier CuAlCl\(_4\) and its adduct with propylene, the molecular volume increments \( V_b \) (in \( \text{cm}^3/\text{mol} \)) can be calculated from the van der Waals radii \( r_{vdW} \) (in \( \text{Å} \)) with:

\[
V_b = 1.3487 r_{vdW}^{4.8428}.
\]

van der Waals radii have been obtained from the molecular simulation tool Spartan and are listed in Table 3.6.

<table>
<thead>
<tr>
<th>element name</th>
<th>vdW radius [Å]</th>
<th>volume increment [cm(^3)/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>2.025</td>
<td>41,103</td>
</tr>
<tr>
<td>Cu</td>
<td>1.572</td>
<td>12,059</td>
</tr>
<tr>
<td>Cl</td>
<td>(1,782)</td>
<td>24.5</td>
</tr>
</tbody>
</table>
Table 3.7: Molar volumes of components

<table>
<thead>
<tr>
<th>Molar Volumes and Volume Increments [cm$^3$/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>propane</td>
</tr>
<tr>
<td>propylene</td>
</tr>
<tr>
<td>carrier</td>
</tr>
<tr>
<td>complex</td>
</tr>
</tbody>
</table>

The diffusion fluxes in the membrane ($j_{i,r}$ and $j_{i,z}$) are calculated with an effective diffusivity approach, where the effective diffusivities are taken to be equal to the diffusion coefficients of each component in the mixture:

$$j_{i,r}^M = -D_{im}^M \frac{\partial c_i^M}{\partial r},$$

$$j_{i,z}^M = -D_{im}^M \frac{\partial c_i^M}{\partial z}.$$  

**Dynamic Viscosity** Calculation of the diffusion coefficients requires the estimation of the dynamic viscosity for the temperature range of interest. For the ionic liquid mixture, the viscosity has not been measured so far. Therefore, the crude assumption is made that the viscosity of the mixture is equal to the viscosity of the neat ionic liquid. To obtain the desired dynamic viscosity $\eta$ the available data point is extrapolated using the Lewis-Squires-Chart [116]:

$$\eta^{-0.2661} = \eta_0^{-0.2661} + \frac{T - T_0}{233},$$

where $\eta$ is the liquid dynamic viscosity in cP at temperature $T$ [K] and $\eta_0$ (63.80 cP) the known value of the liquid viscosity at reference temperature $T_0$ (293.15 K). Extrapolation of the viscosity with the Lewis-Squires-Chart seems to give reasonable results (cf. [117] and 5.1.4).

With this data effective diffusivities can now be calculated and are shown in Table 3.8. They differ from the values taken in the simple model due to the different correlation applied.

**Reaction Modelling in Facilitated Transport:** As already mentioned, the complexation and decomplexation reaction in the respective facilitated transport system is a spontaneous equilibrium reaction, whose kinetics are unknown, but reaction can be assumed to be faster than diffusion. Therefore, the system becomes mass transfer limited. The equilibrium constant will be varied at discrete values in the course of simulation to examine its influence on the selectivity and the total flux. Reaction takes place according to the reaction equation: carrier + propylene $\rightleftharpoons$ complex.

For convenience of the implementation in the modelling software Femlab, the equilibrium constant $K_c$ will be used in the model, which is given as a function of the species'
Table 3.8: Diffusion coefficients in the liquid membrane phase estimated with Geankoplis’ method

<table>
<thead>
<tr>
<th>temperature [°C]</th>
<th>$D_{\text{propane}}$ [m$^2$/s]</th>
<th>$D_{\text{propylene}}$ [m$^2$/s]</th>
<th>$D_{\text{carrier}}$ [m$^2$/s]</th>
<th>$D_{\text{complex}}$ [m$^2$/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>7.65·10^{-11}</td>
<td>8.15·10^{-11}</td>
<td>5.84·10^{-12}</td>
<td>5.04·10^{-12}</td>
</tr>
<tr>
<td>40</td>
<td>1.90·10^{-10}</td>
<td>2.00·10^{-10}</td>
<td>1.48·10^{-11}</td>
<td>1.28·10^{-11}</td>
</tr>
<tr>
<td>60</td>
<td>4.22·10^{-10}</td>
<td>4.49·10^{-10}</td>
<td>3.19·10^{-11}</td>
<td>2.76·10^{-11}</td>
</tr>
<tr>
<td>80</td>
<td>8.10·10^{-10}</td>
<td>8.62·10^{-10}</td>
<td>6.12·10^{-11}</td>
<td>5.28·10^{-11}</td>
</tr>
</tbody>
</table>

concentrations

$$K_c = \left( \frac{c_{\text{complex}}^M}{c_{\text{carrier}}^M c_{\text{propane}}^M} \right).$$

The conversion of $K_c$ to the thermodynamic equilibrium constant $K_a$ and vice versa will be discussed in the final section of this chapter.

Model analysis, which is described in very detail elsewhere [91], has shown that the equation expressing the reaction equilibrium $K_c$ cannot be assigned any (differential, algebraic expressions, parameters) variables by which the model is described. In this form the compartment „membrane phase” and thus the whole model can not be solved. A kinetic approach\(^5\) for the description of equilibrium reaction must be used in order to overcome the problem of the software implementation. The equilibrium constant can be given by the ratio of forward and backward reaction rates and in steady state $\dot{r}_i = 0$:

$$\begin{align*}
\dot{r}_{\text{propane}} &= -k_1 c_{\text{propane}} c_{\text{carrier}} + k_2 c_{\text{complex}} \\
\dot{r}_{\text{carrier}} &= -k_1 c_{\text{propane}} c_{\text{carrier}} + k_2 c_{\text{complex}} \\
\dot{r}_{\text{complex}} &= k_1 c_{\text{propane}} c_{\text{carrier}} - k_2 c_{\text{complex}} \\
\text{with } K_c &= \frac{k_1}{k_2}
\end{align*}$$

Since it is assumed that the reaction equilibrium is reached instantaneously everywhere in the liquid membrane, $k_1$ and $k_2$ must go to infinity. To account for this fact, the reaction rate constants have to be chosen sufficiently large, which can lead to the instability or to non-convergence during the simulation. In order to avoid the expected non-convergence and still account for reaction being faster than diffusion, reaction rate constants with moderate values must be implemented.

**Porosity and tortuosity** Mass transport through the supported liquid membrane is reduced by two factors that must be accounted for. Liquid membrane area that is actually exposed to the feed and permeate side depends on the the porosity of the support. The more

\(^5\)Kinetic approach is justified for common carriers that show either no barrier or the barrier lies far below 20 kJ/mol. It is shown by molecular modelling that activation energy for most carrier systems is non-existent or is well below 20 kJ/mol.
3.3. COMPLEX MODEL

porous the support is, the more active membrane area is available and the higher mass transport can be achieved. Mass transport is also influenced by the tortuosity of the support. Tortuosity factor is one in a simple case, where the cylindrical pores of the support are flooded with membrane phase liquid. Here, the liquid membrane thickness corresponds to the diffusion length. When the pores are not straight, the diffusion length is increased. A porosity factor \( \epsilon \) is introduced in this work to appropriately adjust the available membrane area and hence the diffusive flux:

\[
\dot{j}_i^M = -\epsilon D_{im}^M \frac{\partial c_i^M}{\partial r}.
\]

The support pores in the present model are assumed to have a tortuosity of 1. However, since the membrane thickness is a variable, diffusion length can be assigned different values.

Further Equations

As for the feed phase, additional definitions are required for the treatment of the model:

Molar fractions:

\[
x_i^M = \frac{c_i^M}{c_t^M}
\]

Total concentration:

\[
c_t^M = \sum_i^n c_i
\]

Permeate Phase - Equations of Change

For the modelling of the permeate phase, the equations for the feed phase can be taken. However, different number of components in the mixture and different geometry must be considered. The equations of change must be extended for the species nitrogen, that serves as a sweep gas. As for the feed phase, no reaction takes place in the compartment.

Permeate Phase - Boundary Conditions

Boundary conditions for the permeate phase can be formulated as follows:

1. The fluxes for propane and propylene have to be equal at both sides of the membrane-permeate phase boundary (7), whereas nitrogen is assumed to be not soluble in the liquid membrane (no flux through the phase boundary).

\[
\dot{N}_i^P = \dot{N}_i^M \\
\dot{N}_{N_2}^P = 0
\]

\(^6\)As an example, in liquid membrane support made of sintered spherical particles, tortuosity can be calculated from the support thickness \( l \) and mean radii of spheres \( r \) according to \( \frac{1}{4} \cdot \pi r = \frac{l^2}{2} \)
2. At the sweep gas entry (8), pure nitrogen enters the permeate compartment - the concentrations of all other species are set to zero. Composition of the permeate at the permeate exit (9) are to be calculated.

\[ c_{N_2} = c_{i}^{0,P} \]
\[ c_{i \neq N_2} = 0 \]

3. In axial direction no diffusive flux \( j_{i,z} \) takes place. All axial mass transfer is considered to be convective:

\[ j_{i,z} = 0 \]

This assumption is commonly made in numerical calculations and is reasonable, because axial mass transport is dominated by convection.

4. There is no flux through the module wall (boundary 10):

\[ \dot{N}_i^P = 0 \]

Permeate Phase - Constitutive Equations

Velocity profile The velocity profile for laminar flow in the permeate compartment can be calculated by the application of known correlations [136]. The appropriate modified correlation for an annulus reads:

\[ v_{P}^{z} = \dot{Q}_{avg}^{P} \cdot A \cdot f(r) \quad \text{with} \]
\[ A = \frac{2}{\pi} \frac{R_2^2}{R_3^3} \ln\left(\frac{1}{\kappa}\right) \cdot \frac{1}{\left((1 - \kappa^4) - (1 - \kappa^2)^2\right)} \]

where \( \dot{Q}_{avg}^{P} \) is the average volumetric flow of the permeate. \( \kappa \) denotes the ratio of inner (\( R_2 \)) and outer radius (\( R_3 \)) of the annulus.

\[ \kappa = \frac{R_2}{R_3} \]

The radial component dependency of the velocity is expressed by \( f(r) \), which can be formulated as:

\[ f(r) = 1 - \left(\frac{r}{R_3}\right)^2 + B \ln \frac{r}{R_3} \quad \text{with} \]
\[ B = \frac{1 - \kappa^2}{\ln\left(\frac{1}{\kappa}\right)} \]

Diffusion Diffusion is described with the same effective diffusivity law as it was used in feed phase. However, the diffusion coefficients will have higher values due to the lower overall pressure inside the permeate phase (cf. Table 3.5).
3.3. COMPLEX MODEL

Phase Connections

So far, the three elements of the membrane module are only connected via their boundary conditions at the liquid-gas phase boundaries, where the flux of each component is stated to be equal at both sides of the respective phase boundary. Since constant fluxes do not provide any information on the liquid’s capacity for the dissolved components, vapour-gas equilibria (VLE) at these phase boundaries must be additionally accounted for. This common procedure in chemical engineering often gives sufficiently accurate models with predictive character [37].

The amount of the gas or vapour dissolved in the liquid is often estimated with the simple VLE model, i.e. Henry’s law for ideal fluids, for which the thermodynamically correct form reads [139]

\[ x_{i}^{\text{liquid}} H_{ij} = p x_{i}^{\text{gas}}. \]

Henry’s law states that the amount of gas of species i dissolved in solvent j is proportional to its partial pressure and, in our case, connects the molar fractions of each species in the membrane with their molar fractions in the feed and permeate phase. In addition to the constraint of the constant fluxes perpendicular to the membrane surface, Henry’s law imposes another constraint on the boundary conditions of the equations of change. Both constraints can not be handled at once by any simulation software so far. In the same manner as for the equilibrium reaction, a pseudo kinetic approach is used for description of Henry’s law. The method applied is called a stiff-spring-method [140].

Fluxes at both sides of the membrane phase boundary are set to a value \( N_i \)

\[ \dot{N}^{F/P}_i = \dot{N}^M_i = N_i, \]

which ensures constant fluxes across the boundary. \( N_i \) is further defined as

\[ N_i = M^\infty (r^{F/P}_i p - H x_i), \]

with \( M^\infty \) as an arbitrary chosen high number (e.g. 10^5). Due to the high value of \( M^\infty \) and small fluxes through the membrane, the term \( (r^{F/P}_i p - H x_i) \) is forced to zero. The higher \( M^\infty \), the smaller the numeric error of the constant flux constraint. Problems arise if \( M^\infty \) is chosen to high, possibly leading to numerical divergence, especially at the beginning of the iterative cycles.

The stiff-spring-method is applied at boundaries 4 and 7 for all components that diffuse through the membrane. However, during the implementation process, convergence problems occurs, when the Henry’s law is expressed in term of molar fractions. Better convergence could be obtained by the application of the equation based on molar volume concentrations. Reasons for this behavior could not be determined. The implemented form reads

\[ N^{F/P,M}_i = M^\infty (r^M_i - \frac{1}{H_{c,i}} r^{F/P}_i). \]
The concentration related Henry coefficient $H_{c,i}$ is defined as

$$H_{c,i} = \frac{H_{ij}}{c_i RT}.$$ 

The Henry coefficients of all components in ionic liquid [BMIM]$^+$[BTA]$^-$ were measured for a temperature of 20°C (cf. experimental section and [50]). For a model that should predict the separation performance depending on the system temperature, realistic data of Henry coefficients is needed. Solubilities were determined using the molecular modelling software. The results are listed in Table 3.9.

<table>
<thead>
<tr>
<th>Henry Coefficient [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature [°C]</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>40</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>70</td>
</tr>
<tr>
<td>80</td>
</tr>
<tr>
<td>90</td>
</tr>
<tr>
<td>100</td>
</tr>
</tbody>
</table>

The interpolation of the data points yields the following equations for the Henry coefficients [MPa] as a function of temperature $T$ in [K] of component $i$ in ionic liquid [BMIM]$^+$[BTA]$^-:$

$$H_{\text{propane}} = -3, 4147 \cdot 10^{-6} T^3 + 3, 1879 \cdot 10^{-3} T^2 - 6, 0431 \cdot 10^{-1} T + 7, 6353$$

and

$$H_{\text{propylene}} = -2, 3762 \cdot 10^{-6} T^3 + 2, 8040 \cdot 10^{-3} T^2 - 9, 1148 \cdot 10^{-1} T + 90, 5706.$$ 

The solubility of nitrogen is more than 15 times smaller than the solubilities of other components and will only be found in traces in the liquid membrane. Its concentration can be neglected in the present model.

Experimental solubility data (vide supra; [117]) differ from the results obtained at 20°C by COSMOtherm as this is shown in Table 3.10, where solubility data is expressed in terms concentration referred Henry’s coefficient (mbar m$^3$/mol; infinite dilution in pure ionic liquid with density of 1470 kg/m$^3$ was assumed).
Table 3.10: Experimental and Cosmo therm Henry coefficients at 20°C

<table>
<thead>
<tr>
<th>component</th>
<th>COSMOtherm Henry coefficient [mbar m$^3$ mol$^{-1}$]</th>
<th>experimental Henry coefficient [mbar m$^3$ mol$^{-1}$]</th>
<th>adjustment factor $\Psi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>propylene</td>
<td>51.36</td>
<td>13.296</td>
<td>0.259</td>
</tr>
<tr>
<td>propane</td>
<td>12.59</td>
<td>7.444</td>
<td>0.591</td>
</tr>
</tbody>
</table>

In the model implementation, COSMOtherm data is brought in line with experimental solubilities by means of an adjustment factor $\Psi$:

$$\Psi = \frac{H_{\text{experimental}}}{H_{\text{COSMOtherm}}}.$$  

Now, we have gathered all the information on the model’s individual components and can turn to the model implementation, which will be shortly presented next.

### 3.3.3 Implementation in Femlab

The derived models are independent of any software platform. However, I have decided to perform simulations with the simulation software Femlab, which seems to be suitable for the treatment of a wide variety of engineering problems.

**Simulation Tool Femlab**

For the better understanding of the implementation of the derived model equations, it is necessary to introduce some features of Femlab simulation software. For detailed information it should be referred to the Femlab user guide [140].

Femlab is an equation based modelling and simulation tool. In contrast to the sequential based simulation software, where in a repeated cycles each part$^7$ of the model is the input to the next part until the convergence of the complete model is achieved, all equations are assembled in one step, which leads to a system of partial differential equations (PDEs) and algebraic equations. Together, they form a partial differential and algebraic equation system (PDA). When solving a PDA, Femlab uses the finite element method (FEM). The software runs the finite element analysis together with adaptive meshing and error control using a variety of numerical solvers, among which the user can choose the appropriate one. The great advantage of Femlab lies in its ability to solve all kinds of PDA systems. In this way, the user is not limited to a specific application like in a fluid dynamics simulation, but can use rather different kinds of PDE’s, which can be combined to form a complete model of a system. Femlab calls this multiphysics modelling. Some predefined PDE’s for common and reoccurring problems already exist as a part of the program in form of modules. One example is the Navier Stokes equation with constant density and viscosity.

---

$^7$Each part, of course, must for itself be brought to convergence in its own subroutines.
Femlab can be used either as a tool for steady-state analysis, i.e. stationary problems, or for dynamic, i.e. transient, instationary simulation.

**Modelling Process in Femlab**

Modelling and simulation with Femlab is generally performed in six steps. These steps can be summarised:

- geometry definition
- meshing
- implementation of the mathematical formulations
- definition of the solver parameters
- solving of PDA (calculation)
- postprocessing

First is the implementation of a model’s geometry. This can be done either inside the Femlab environment (GUI) or by importing of CAD drawings. In this work, the relatively simple geometry of the membrane separation unit was created by Femlab GUI. Geometries can be defined in 1, 2 or 3 dimensions and either in cartesian or cylindrical coordinates. Geometry is an image of the real geometry. If equations are intended to be valid not for the entire geometry but only for specific areas of the geometries, it is necessary to define one or more geometry subdomains. The three phases feed, membrane and permeate will be made subdomains of the membrane module in this model.

After the geometry and subdomains have been defined, the next step is to create a mesh of finite elements (FE) consisting of discrete volume (or area) elements in every subdomain. As with all simulation programs, there always is a trade-off between the quality of the numerical solution, which is obtained with a high number of FE, and the computational time. The compromise must be chosen in terms of CPU speed and available amount of memory. The mesh can be automatically defined and refined by Femlab automatically. If a customized mesh is wanted it can also be defined manually.

The most time consuming part of the implementation process is the implementation of the actual mathematical model, which I have described in previous section. Femlab distinguishes between the PDE’s with the corresponding initial and boundary conditions, analytical equations (explicitly defined expressions), that can be defined either for an entire geometry or for one or more subdomains and finally, the constants, which are always defined for an entire geometry.

The last three steps in the Femlab simulation process are the definition of solver parameters (for obtaining desired stationary or instationary solutions), running the solving procedure and after a solution is reached, the postprocessing of the simulation. The post-processing environment also comprises graphical visualization tools for the analysis of the simulation results.
3.3. COMPLEX MODEL

Implementation

Geometry

Due to the symmetry of the membrane module the representative simulation can be performed with the longitudinal cut through the half of the module’s geometry. This 2-D representation reduces memory demand and computing time. For the most common engineering problems geometry can be implemented in SI units in 1:1 ratio. However, if large differences in the size (volume or area) between the elements within the complete geometry exist, this leads to an excessive amount of finite elements and nodes in the larger elements (in our case, the permeate and the feed compartments of the membrane module are large in comparison to the dimensions of the liquid membrane, cf. Table 3.3), since an accurate calculation requires a mesh element smaller than the membrane thickness. Although the element size can be adjusted from the smallest element inside the liquid membrane to the feed and permeate compartments, where the gradients are expected to be smaller, the number of elements will still be very large if the complete 1:1 geometry of the module is implemented. Therefore, the membrane module geometry and the model equations are scaled in z-direction (axis of symmetry) according to

\[
\frac{z_{\text{simulated}}}{\varphi z_{\text{real}}} \quad \text{and} \quad \frac{dz_{\text{simulated}}}{\varphi dz_{\text{real}}}
\]

For the simulation a scaling factor \( \varphi \) of 20 is used for the facilitated transport model and 11.2 for solution diffusion-model.

The geometry is build by two rectangles, which define the three compartments feed, membrane and permeate, whereas the overlapping area of the two rectangles builds the membrane (cf. Figures 3.6 and 3.7). Geometry implementation data is listed in Table 3.11.

<table>
<thead>
<tr>
<th>Table 3.11: Geometry implementation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>object number</strong></td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td><strong>solution-diffusion model</strong></td>
</tr>
<tr>
<td>R1</td>
</tr>
<tr>
<td>R2</td>
</tr>
<tr>
<td><strong>facilitated transport model</strong></td>
</tr>
<tr>
<td>R1</td>
</tr>
<tr>
<td>R2</td>
</tr>
</tbody>
</table>

Meshing

The smallest mesh elements are defined at the liquid-gas phase boundary and in the membrane, where the steepest gradients in the modelling of the mass transport are expected. The number of the finite elements should be below 10000 in order to ensure computability. Across the membrane, at least 6 to 8 mesh points must be realized in order to have a smooth and sufficiently accurate solution.
A meshing example for a membrane thickness of 200 \( \mu \text{m} \) is shown in Figure 3.7. The smallest cell size boundary is approximately \( 5 \cdot 10^{-4} \) m with an element growth rate of 1.3. The total number of the finite elements in this case amounts to total 6917.

Figure 3.7: Mesh resolution - a screen shot of the Femlab GUI during meshing procedure

If changes are made to the geometry, e.g., if the membrane thickness is varied, the mesh needs to be redefined for each such calculation. Mesh parameters are therefore not fixed.

**Implementation of Mathematical Formulations**

The whole model can be implemented with predefined Femlab modules. The coefficients of differential equations (like diffusion coefficients) can be directly formulated into the equation coefficients of general or coefficient form, where applicable. The implementation of the differential balances and boundary conditions is summarized in Tables 3.12 and 3.13.

All the analytic model expressions are considered in Femlab without any changes of the equations presented above (cf. 3.3.2). Constants, where applicable, will also not be treated any further. The concentration initial conditions are chosen arbitrarily in such a way that the convergence is more likely to occur. The diffusion and convective velocity in \( z \)-direction are scaled according to the scaled geometry.

Along with the Femlab modules some predefined boundary conditions are also provided.
Table 3.12: The parameters of the feed element and the permeate element

<table>
<thead>
<tr>
<th>module name</th>
<th>module parameters</th>
<th></th>
<th>reaction R</th>
<th>r-velocity</th>
<th>z-velocity</th>
<th>initial value</th>
</tr>
</thead>
<tbody>
<tr>
<td>convective &amp; diffusion module</td>
<td>$D_{PA,eff}^{F/P} r z$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$\frac{v_{r/p}}{\text{scale}}$</td>
<td>$c_{PA}$</td>
</tr>
<tr>
<td>propane</td>
<td>$D_{PA,eff}^{F/P} r z$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$\frac{v_{r/p}}{\text{scale}}$</td>
<td>$c_{PA}$</td>
</tr>
<tr>
<td>propylene</td>
<td>$D_{P,E,eff}^{F/P} r z$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$\frac{v_{r/p}}{\text{scale}}$</td>
<td>$c_{PE}$</td>
</tr>
</tbody>
</table>

These are:

- symmetry - all gradients normal to the boundary are set to zero.
- concentration - the concentration of a species is fixed at a certain value at the boundary.
- flux - the flux across the boundary is fixed.
- convective flux - the diffusive flux is set to zero (only available in the „convective & diffusion” module).

The symmetry boundary actually equals to the flux boundary condition with a flux equal to zero. All boundary definitions are shown in Tables 3.14 and 3.15. Depending on the boundary type either concentration (c) or flux (N) is defined, whereas a (CF) stands for convective flux and (SYM) for symmetry boundary conditions. The boundary numbering is taken from Fig. 3.6.

### 3.3.4 Mass Transfer Simulation - Results

Simulations are carried out for the solution-diffusion model and for the facilitated transport model. The feed stream in the experiments, i.e. propylene/propane mixture was taken from a gas bottle as vapour with the components ratio of 50:50 vol%.

**Solution-Diffusion Separation**

The model used for the simulation is the facilitated transport model, where the reaction constants for the carrier reaction and the carrier concentration are set to zero. Temperature is varied from 0°C to 70°C. In this temperature range the ionic liquid is stable inside the membrane pores without liquid loss due to thermal decomposition. Membrane porosity is assumed to be 0.25 with an estimated liquid membrane thickness of 284 µm.
Table 3.13: The parameters of the membrane element

<table>
<thead>
<tr>
<th>module name</th>
<th>module parameters</th>
<th>reaction</th>
<th>initial value</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion module</td>
<td>diffusion D</td>
<td>$r \ z$</td>
<td></td>
</tr>
<tr>
<td>solution-diffusion</td>
<td>$\epsilon D_{PA,eff} \frac{M_{PA}}{x} \frac{2}{x}$</td>
<td>0</td>
<td>$c_{PA}$</td>
</tr>
<tr>
<td>propane</td>
<td>$\epsilon D_{PE,eff} \frac{M_{PE}}{x} \frac{2}{x}$</td>
<td>$-k c_{PE} \ = \ 0$</td>
<td>$c_{PE}$</td>
</tr>
<tr>
<td>propylene</td>
<td>$\epsilon D_{PE,eff} \frac{M_{PE}}{x} \frac{2}{x}$</td>
<td>$-k c_{PE} \ = \ 0$</td>
<td>$c_{PE}$</td>
</tr>
<tr>
<td>facilitated transport</td>
<td>$\epsilon D_{CA,eff} \frac{M_{CA}}{x} \frac{2}{x}$</td>
<td>$k_2 c_{CX}^M - k_1 c_{CA} c_{PE}$</td>
<td>$c_{CA}$</td>
</tr>
<tr>
<td>carrier</td>
<td>$\epsilon D_{CA,eff} \frac{M_{CA}}{x} \frac{2}{x}$</td>
<td>$k_2 c_{CX}^M - k_1 c_{CA} c_{PE}$</td>
<td>$c_{CA}$</td>
</tr>
<tr>
<td>complex</td>
<td>$\epsilon D_{CX,eff} \frac{M_{CX}}{x} \frac{2}{x}$</td>
<td>$-k_2 c_{CX}^M + k_1 c_{CA} c_{PE}$</td>
<td>$c_{CA}$</td>
</tr>
</tbody>
</table>

Selectivity

Selectivity and permeability are of major importance for the separation process. As mentioned in the introduction, selectivity can be defined as the ratio of the permeate to the feed side molar fraction ratio of propylene to propane. Due to the lower solubility of propane, the separation is more selective towards propylene. Figure 3.8a displays this behavior. Simulated selectivity decreases more or less linearly with increasing temperature. At 20°C selectivity is as high as 4.3 and drops to 3.5 at 60°C. Here, Henry coefficients values were taken directly from COSMOtherm.

For the temperature range of interest the selectivity of the solution-diffusion separation system has been experimentally examined. Although a decrease in selectivity with increasing temperature has been observed, selectivity has been found to be lower, i.e about 1.9 at 20°C and 1.7 at 60°C.

The poor ability of the model for the prediction of selectivity more accurately can be tracked back to the calculated COSMOtherm solubilities. It can be seen in Figure 3.8a that selectivity is directly proportional to the Henry coefficient ratio. A very accurate improvement was achieved by the simple adjustment of COSMOtherm’s Henry coefficients to the measured values with the correction factor $\Psi$ that was introduced above (cf. Table
3.3. COMPLEX MODEL

Table 3.14: Boundary conditions - solution-diffusion model

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed Boundary</th>
<th>Membrane Boundary</th>
<th>Permeate Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1  2  3  4</td>
<td>Comp.  4  5/6  7</td>
<td>Comp.  7  8  9  10</td>
</tr>
<tr>
<td>Propane</td>
<td>SYM ( c = c_{PA}^{e,r} ) CF ( N = M^\infty (c_{PA}^M - H_{PA}^{-1}c_{PA}^F) ) ( N = M^\infty (c_{PE}^M - H_{PE}^{-1}c_{PE}^F) )</td>
<td>SYM ( N = M^\infty (c_{PA}^M - H_{PA}^{-1}c_{PA}^F) ) ( N = M^\infty (c_{PE}^M - H_{PE}^{-1}c_{PE}^F) )</td>
<td>SYM ( N = M^\infty (c_{PA}^M - H_{PA}^{-1}c_{PA}^F) ) ( N = M^\infty (c_{PE}^M - H_{PE}^{-1}c_{PE}^F) )</td>
</tr>
<tr>
<td>Propene</td>
<td>SYM ( c = c_{PA}^{e,r} ) CF ( N = M^\infty (c_{PA}^M - H_{PA}^{-1}c_{PA}^F) ) ( N = M^\infty (c_{PE}^M - H_{PE}^{-1}c_{PE}^F) )</td>
<td>SYM ( N = M^\infty (c_{PA}^M - H_{PA}^{-1}c_{PA}^F) ) ( N = M^\infty (c_{PE}^M - H_{PE}^{-1}c_{PE}^F) )</td>
<td>SYM ( N = M^\infty (c_{PA}^M - H_{PA}^{-1}c_{PA}^F) ) ( N = M^\infty (c_{PE}^M - H_{PE}^{-1}c_{PE}^F) )</td>
</tr>
</tbody>
</table>

3.10).

**Permeability**

Permeability of the membrane separation is further characterized by its permeability. I define here the permeability as the transmembrane volumetric flux at standard state (20°C, 1 bar) per membrane area and transmembrane partial pressure drop. In our particular case transmembrane partial pressures of propylene and propane are equal (1.5 bar) and sum up to the total transmembrane pressure difference (3 bar)

\[
P = \frac{V^\circ}{A \Delta p_{\text{trans}}}.\]

Membrane area is defined with the inner diameter of the liquid membrane in the porous support, which is 1.9 mm. Simulated and experimental permeabilities for a membrane thickness of 284 µm in the temperature range are given in Figure 3.8b. Experimentally determined permeabilities for propylene and propane are about one order of magnitude higher than their simulation counterparts. In the simulation the component solubilities have been implemented with the adjusted Henry coefficients. According to solution-diffusion model permeability is determined by both solubilities and diffusion coefficients of the components in the ionic liquid. Therefore, it can be assumed that the Geankoplis’ method by which the diffusion coefficients were determined is not adequate for ionic

---

8On the permeate side, partial pressure of zero is assumed, since the nitrogen sweep is in orders of magnitude higher than the flux through the membrane. Even if there exists a partial pressure of 100 mbar, the error in the permeability value will be lower than 6%
Table 3.15: Boundary conditions - facilitated transport

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed Boundary</th>
<th>Membrane Boundary</th>
<th>Permeate Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Component</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Propane</td>
<td>SYM</td>
<td>$c = c^f_{PA}$</td>
<td>CF</td>
</tr>
<tr>
<td>Propene</td>
<td>SYM</td>
<td>$c = c^f_{PE}$</td>
<td>CF</td>
</tr>
</tbody>
</table>

liquids. The values obtained lie at approximately $8 \cdot 10^{-11} \text{ m}^2\text{s}^{-1}$, which is the range of diffusion coefficients in dense polymers and solids. More realistic results can be achieved by arbitrary manipulation of the liquid diffusion coefficients, which were multiplied with an adjustment factor of 10. Please note that whereas the diffusion coefficients in the simple model, which were calculated by modified Geankoplis’ method are too high ($10^{-9} \text{ m}^2\text{s}^{-1}$), applying the method exactly without adjustments yields too low diffusion coefficients ($10^{-11} \text{ m}^2\text{s}^{-1}$). In the experimental section (cf. Table 5.12), the order of magnitude of diffusion coefficients for propane and propylene lies between the two obtained by estimation methods ($10^{-10} \text{ m}^2\text{s}^{-1}$) and corresponds with the values corrected by this arbitrary adjustment. Permeability results of the simulations with adjusted diffusivities and solubilities are shown in Figure 3.8b). The simulated permeability for propylene and propane corresponds well with experimentally determined data, although temperature dependence in simulations is stronger than experimentally observed.

It has to be noted again that the solubility and the diffusivity have contrary influences on permeability. An increase in temperature results in lower solubilities, but in higher diffusivities. From the results obtained it can be obviously summarised that with respect to permeability the effect of an increase in diffusivities outdoes the decrease on solubilities with increasing temperature. When the diffusion coefficients are within the same order of magnitude, solubilities crucially influence the selectivity, which decreases with increasing temperature.

The separation performance is also influenced by the membrane thickness and its porosity. For the detailed treatment of this problem it should be referred to [91], where it was found
Figure 3.8: Simulated and experimentally determined selectivity and permeability

- in line with classical understanding of membrane separations - that the permeability is inversely proportional to the membrane thickness and linearly dependent on porosity.

**Conclusions on the Solution-Diffusion Separation Model**

Selectivity prediction of the model is accurate for temperatures from 20°C to 60°C, when solubility is appropriately adjusted to match experimental data. Realistic predictions for permeability can be made in the range from room temperature to 40°C, when diffusivity is adjusted. For higher temperatures a good estimate of actual selectivity can be expected from simulations. In contrast, prediction is poor for the permeability because of the functional runaway of the temperature dependance of the solubility, which should be experimentally determined in the whole temperature range of interest.

**Facilitated Transport Separation**

Simulations have been carried out for a temperature range from 0°C to 100°C with varying equilibrium constant $K_c$. Solubilities of propane and propylene were again determined by COSMOtherm and have been adjusted to experimental selectivity data as described previously. Adjustment of the diffusion coefficients has not been applied, since there is no information available on diffusivities of the carrier and the propylene-carrier complex. In order to deal with consistent data sets, all diffusion coefficients were calculated by the same method. Slightly different membrane geometry and operating conditions were used. Membrane inner radius was set to 0.5 mm, membrane thickness to 200 µm and membrane porosity was assumed to be 0.7. The nitrogen sweep gas stream was set to 12 ml/min. The feed stream with equimolar propylene and propane composition entered the membrane module at 4 ml/min.

$K_c$ is taken to be a constant at given temperature. Certainly, one could model the equilibrium with forward and backward reactions according to Arrhenius-ansatz. However, it could be shown that in such a model convergence stability of the simulation decreases. van’t Hoff-ansatz was not tested.
Selectivity and Flux in Facilitated Transport Model

Selectivity in the complex facilitated transport model is shown in Figure 3.9a. Analogously to the selectivity in the simple model, an increase in the equilibrium constant results in the selectivity increase until a maximum is reached. This holds for every temperature. With further increase of the equilibrium constant the selectivity then drops back to the initial value, which can be compared to that of the solution-diffusion model. The highest selectivity is found at an equilibrium constant $K_c$ equal to $0.2 \text{ m}^3/\text{mol}$. An increase in temperature also enhances flux facilitation. However, as result of low (and convergent) gas solubilities at high temperatures there is also an optimum in respect to the temperature (here $50^\circ\text{C}$). This temperature dependence was, however, not closer examined.

![Figure 3.9: Propylene/propane selectivity (ratio of pure fluxes) and propylene permeability as a function of temperature and equilibrium constant $K_c$.](image)

Propane flux (permeability) is independent of the applied equilibrium constants and is constant for the given temperatures. Figure 3.9b shows the propylene permeability depending on temperature and equilibrium constant $K_c$. Very low and very high equilibrium constants ($K_c \rightarrow 0$, $K_c \rightarrow \infty$) lead to a non-facilitated propylene flux. For high values of $K_c$ free carrier molecules in the entire liquid phase are not available, whereas no complex is built at all if the equilibrium constant is low. The flux is noticeably facilitated for an equilibrium constant values between $0.01$ and $1 \text{ m}^3/\text{mol}$. The equilibrium constant value, where the propylene transmembrane flux is maximized, lies approximately at the of $0.2 \text{ m}^3/\text{mol}$ and is more or less independent of temperature.

Figure 3.10 displays the flux enhancement in terms of the facilitation factor. Higher temperatures do not only increase the diffusive total flux, but also enhance the contribution of the facilitated transport. The facilitation factor reaches its maximum like propylene permeability for all considered temperatures between $K_c$ values of $0.1$ and $0.3 \text{ m}^3/\text{mol}$. In the current work, the maximum facilitation factor of $2.4$ was obtained. Simulation with the same model [91] using similar values of physical properties and variables gave slightly higher value facilitation factor of approximately $3.5$, but precisely in the same $K_c$ range.
3.4 On chemical equilibrium

3.3.5 Conclusions on Simulations

The results of the simulations can be summarized as follows. An increase in temperature increases the overall permeabilities of the liquid membrane. Selectivities decrease with temperature and are entirely dependant on the ratio of individual components’ solubilities, i.e. on the ratio of the respective Henry’s coefficients. The influence of diffusion coefficients on selectivity, while being in the same order of magnitude, is marginal. The calculated selectivities and permeabilities can be brought in line with experiments only by the adjustment of Henry’s coefficients and diffusion coefficients.

The same general trend holds for the facilitated transport model, where, due to the same restrictions, the exact selectivity and permeabilities can not be predicted. The selectivity increases with temperature and reaches maximum at approximately 50°C and decreases at higher temperatures. However, it should be more carefully examined with respect to the global maximum. The effect has nothing to do with equilibrium constant, but is solely dependant on the temperature dependant solubilities. The most important fact for the purpose of this work is that the maximum for the propylene flux and thus for the facilitation factor is found for equilibrium constant values $K_c$ between 0.1 and 0.3 $m^3/mol$ and is more or less independent of temperature. This equilibrium constant, which is an order of magnitude greater that the one derived from the analytical model, will be used for the estimation of the thermodynamic equilibrium constant $K_a$. For the understanding of how the two equilibrium constant relate to each other, the necessary basic of thermodynamics must be introduced, which is the subject of the next section.

3.4 On chemical equilibrium

Although all equilibrium thermodynamics is defined in an unambiguous manner, chemical equilibrium constant is encountered in several different formulations in practise. In particular, formulations as they are used by chemical engineers and by chemists can be distinguished. Whereas in chemistry the use of concentration based equilibrium constant
3. MASS TRANSPORT MODELLING

$K_c$ is more widespread, in chemical engineering - more correctly - thermodynamic equilibrium constant $K_a$ is applied\(^{10}\). The chemical equilibrium constant, which is expressed in concentration units, may be used in reactor design for simple reactions, but is useless for the thermodynamic evaluation. This fact makes it very difficult to compare different experimental or theoretical results reported in the literature. Nevertheless, with the knowledge of physical properties of the system it is possible to make the two formulations comparable.

3.4.1 Enthalpy of Reaction

Reactants and reaction products in a closed system hold different binding energies. When bonds are broken and build anew a change of energy is involved, which usually occurs as thermal energy \([142]\).

The enthalpy change associated with chemical reactions, $\Delta_r H$, can be viewed as the total enthalpy of the products minus the total enthalpy of the reactants:

$$\Delta_r H = H_{\text{prod}} - H_{\text{react}}.$$  

For an exothermic reaction $\Delta_r H < 0$, energy is evolved as heat in the course of the reaction. For an endothermic reaction $\Delta_r H > 0$, energy as heat must be supplied to drive the reaction. The enthalpy change, $\Delta_r H$, also depends upon the change of number of mols of the reactants and products. In order to have a common reference state, the standard reaction enthalpy is introduced, which is denoted by $\Delta_r H^\circ$ and refers to the enthalpy change associated with one mol of a specified reagent when all reactants and products are in their standard states. The standard state for a gas is the equivalent ideal gas at a pressure of one bar and at the temperature of interest, whereas for a liquid it refers to the normal state of the liquid at one bar and at the temperature of interest. $\Delta_r H$ is an extensive quantity, whereas $\Delta_r H^\circ$ is an intensive quantity. The advantage of this terminology is that it removes the ambiguity of how the balanced reaction corresponding to an enthalpy change is written \([143]\).

The standard molar enthalpy of formation, $\Delta_f H^\circ$, is particularly useful. This intensive quantity is the standard reaction enthalpy for the formation of one mol of a molecule from its constituent elements. The superscript „zero“ denotes that all reactants and products refer to their standard states. For each pure element in its most stable form at one bar and at the temperature of interest, $\Delta_f H^\circ$ is set equal to zero. Thus, standard enthalpies of formation of compounds are given relative to the elements in their normal physical states at one bar, (this classical thermodynamical definition of the „zero of energy“ is different from that in the quantum mechanics, where it is taken to be the difference of energies of individual atoms at infinite distance and the compound built thereof, cf. B.3). For many compounds, $\Delta_f H^\circ$ are tabulated \([16, 116, 143, 141]\). It is not necessary to tabulate values

\(^{10}\)Most of these different formulations for chemical equilibrium constants (e.g. $K_p$, $K_x$, etc.) stem from historical context and relate to the nature of examined systems as well as to the investigation methods. None formulations will yield the same numerical values \([141]\), but the treatment of extremely diluted solutions is more simple.
of $\Delta_r H^0$ for all conceivable reactions. It is sufficient to tabulate values of this parameter only for the reactions that involve the formation of a compound from its elements. Where the values are not available, so called Hess’s Law may help to calculate the enthalpy of unknown compounds and enthalpy changes associated with chemical reactions, where applicable. Several group contribution methods are also available [116]. In general, we obtain the enthalpy changes according to the following equation:

$$\Delta_r H = \sum \nu_i \Delta_i H^0_i .$$

The problem of data compilation is further simplified by the fact that it is not necessary to record $\Delta_f H^0$ at all temperatures. The convention that is commonly accepted in engineering practise today, is reporting values of standard enthalpies of formation at 298,15 K [144]. The calculation of $\Delta_r H^0$ at finite temperature $T$ is reduced to determination of $\Delta_f H^0$ at 298,15 K and to the adjustment of the value taking into account the effect of the temperature as given by Kirchhoff’s law [145]:

$$\Delta_r H^0 (T) = \Delta_r H^0_0 + \int_{298,15}^{T} \Delta c_p(T) dt \quad \text{with} \quad \Delta c_p(T) = \sum \nu_i c^0_{p,\text{m},i}(T).$$

c$^0_{p,\text{m},i}(T)$ represent the molar heat capacity of the pure component $i$ at the temperature $T$ and atmospheric pressure.

### 3.4.2 Gibbs Free Energy and Chemical Potential

Fundamental thermodynamics states that the (absolute) Gibbs free energy change of a given system is related to the chemical potentials of the participating species [16]:

$$dG^* = SdT + Vdp + \sum \mu_i dn_i$$

At constant temperature and pressure the expression for Gibbs free energy reduces to:

$$dG^* = \sum \mu_i dn_i$$

All $dn_i$ can be replaced by their conversion values $\xi$:

$$d\xi = \frac{dn_i}{\nu_i},$$

and by consideration of the stoichiometric coefficients $\nu_i$ for the reaction one obtains :

$$\frac{dG^*}{d\xi} = \sum \nu_i \mu_i .$$

The chemical potentials $\mu_i$ depend on the composition of the system, on the the temperature and on the pressure:

$$\mu_i (p, T) = \mu_i^0 + RT \ln \frac{f_i}{f_i^0} = \mu_i^0 + RT \ln \frac{a_i}{a_i^0} ,$$
where the composition of the mixture is expressed as fugacity for gases and as activity in liquids.

As a chemical reaction advances in either direction by \( d\xi \), the change in the composition of the reaction mixture results in a change of the free energy of the system, \( dG \). The (positive or negative) gradient of the Gibbs free energy in dependence of the extent of reaction gives a measure for the spontaneity of reaction - the steeper gradient indicates that the reaction is far from the steady state equilibrium. Chemical equilibrium is reached when the Gibbs free energy becomes minimal [146], i.e. gradient is zero at equilibrium state. (When the composition of a reacting system does apparently not change anymore, it is in dynamic equilibrium, i.e. direct and reverse reaction take place at the same speed.)

The combination of the last two equations with an assumption of zero gradient yields the well known expression for the thermodynamical chemical equilibrium constant \( K \) (\( K_f \) or \( K_a \)) in terms of the standard Gibbs energy change of reaction \( \Delta r G^0 \) [145]:

\[
\Delta_r G^0 = \sum \nu_i \Delta f_i G^0 = \sum \nu_i \mu_i^0 = -RT \sum \ln \left( \frac{f_i}{f_i^0} \right)^{\nu_i} = -RT \ln K
\]

where the standard pressure is denoted by the superscript 0. Just in the same manner as standard enthalpies of formation, the standard Gibbs free energies (of formation!) are also tabulated for many compounds. They can be estimated by group contribution methods [116], where no data is available.

Due to the exponential character of the equation, small errors in estimating \( \Delta_r G^0 \) yield large errors in \( K \), therefore care has to be taken when using the relationship\textsuperscript{11}.

The temperature dependence of the equilibrium constant is given by the van’t Hoff equation:

\[
\frac{d \ln K}{dT} = \frac{\Delta_r H^0}{RT^2}
\]

The heat of reaction is often assumed to remain constant in the temperature range under consideration, and the integrated form of van’t Hoff equation reads:

\[
\ln K(T) = \ln K(T_0) - \frac{\Delta_r H^0}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)
\]

In order to solve this equation for unknown \( K(T) \), the equilibrium constant at at least one defined temperature has to be known. If the heat of reaction changes with temperature, it has to be determined by Kirchhoff’s law. The temperature dependance of the heat capacity of the mixture may be approximated by summing up the individual heat capacities of each component.

The equilibrium constant at an arbitrary temperature may be calculated by evaluating the Gibbs energy change of reaction from the entropies and enthalpies of the components

\textsuperscript{11}It is recommended to cross-check all available data from different sources. However, consistent data from group contribution methods or quantum chemical calculations may provide better results than tabulated values.
3.4. ON CHEMICAL EQUILIBRIUM

according to

\[ \Delta_r G^0 (T) = \Delta_r H^0 (T) - T \Delta_r S^0 (T) \, . \]

The absolute entropies of compounds may be used, since the standard-state entropies of the elements cancel out [116].

\[ \Delta_r S^0 (T) = \sum_i \nu_i \Delta S^0_{f,i} (298 K) + \sum_i \int_{298}^{T} \frac{\nu_i c^0_{p,i}}{T} dT \]

Data and estimation methods are mostly available for the ideal gas state. In order to evaluate the equilibrium constant in the liquid phase, one has to subtract the enthalpies of vaporization from the gas state values. For ionic liquids or other compounds with non-measurable or negligible vapour pressures (e.g. carrier compounds decompose readily well below vaporisation temperatures and pressures) this might be considered to be unsurmountable obstacle.

3.4.3 Equilibrium Constant

Thermodynamic equilibrium constant is formulated by rearranging the Gibbs free energy expression

\[ \Delta_r G(T) = -RT \ln K(T) \quad \Rightarrow \quad K(T) = e^{-\frac{\Delta_r G(T)}{RT}} . \]

The most general postulations of the thermodynamical equilibrium constant according to the Law of Mass Action (Le Chatelier Principle) read

\[ K = \sum \left( \frac{f_i}{\gamma_i \phi_s^i P^s_i} \right)^{\nu_i} = \sum \left( \frac{a_i}{x_i} \right)^{\nu_i} . \]

Here, the fugacities \( f_i \) are usually correlated to the mol-fractions \( x_i \) of the components in the mixture by:

\[ f_i = x_i \gamma_i \phi_s^i P^s_i , \]

where \( \gamma_i \) is the activity coefficient of component \( i \) in the mixture, \( \phi_s^i \) is the fugacity coefficient at given vapour pressure and \( P^s_i \) is the vapor pressure of the pure component \( i \)\(^{12} \). Alternatively, more appropriate for use in the liquid mixtures (with very low vapor pressures), activities can be simply defined by

\[ a_i = x_i \gamma_i , \]

where again \( \gamma_i \) is the activity coefficient of component \( i \) in the mixture.

\(^{12}\)These equations were originally developed for the gas phase only and can be sometimes applied for very dilute solutions. For ionic liquids, however, vapour pressure is often considered to be unity, since no better approach has been developed so far.
The equilibrium constant in terms of concentration can be written as

\[ K = \sum \left( \frac{c_i}{c_i^0} \right)^{\nu_i}. \]

Please note that \( f_i^0 \) and \( c_i^0 \) are by their definition chosen in such a way that they are unity. Activity coefficients can be evaluated by UNIQUAC method [145, 116], where the necessary increments are available. If this is not possible, COSMO\textit{therm} can be used. COSMO\textit{therm} [114] also seems to be the only method so far that can deal with charged systems like ionic liquids.

**Case Study: Conversion of \( K_c \) to \( K_a \)**

In our previous considerations we have derived the „effective“ concentration based equilibrium constant \( K_c \) for the carrier reaction. This means that its numerical value can be taken as it is\textsuperscript{13}.

The concentrations of the species in the membrane phase can be chosen arbitrarily, since they do not influence the equilibrium constant. However, I will try to stick to those values used in simulations. Initial carrier concentration amounts to 1000 mols/m\(^3\). An assumption is made on concentration of propylene in the liquid membrane. According to solution-diffusion model the concentration falls linearly with the membrane thickness being higher at the feed phase and lower at the permeate phase boundary. In the facilitated transport, the overall propylene concentration in membrane is higher than in the solution-diffusion model [91]. The mean concentration of 100 mol/m\(^3\) is a reasonable estimation as initial value (cf. Table 3.2). With known concentration based equilibrium constant, all concentrations can be calculated (propylene, carrier, complex) according to:

\[ K_c = 0,2 = \frac{c_{\text{complex}}}{c_{\text{propylene}} \cdot c_{\text{carrier}}}. \]

Only initial conditions are known, where \( c_{\text{complex}} \) is zero. The above equation is rearranged and solved for the concentration \( c_{\text{reacted}} \):

\[ K_c = 0,2 = \frac{c_{\text{complex}} + c_{\text{complex,reacted}}}{(c_{\text{propylene}} - c_{\text{propylene,reacted}}) \cdot (c_{\text{carrier}} - c_{\text{carrier,reacted}})} , \]

where \( c_{\text{complex,reacted}} = c_{\text{propylene,reacted}} = c_{\text{carrier,reacted}} \) due to the simple stoichiometry.

Molar fraction \( x_i \) is defined as the ratio of mol of component i and the total mol of the mixture. Concentration is usually given in mol of component i per liter of mixture but\textsuperscript{13}Activity coefficients \( \gamma_i \) are not required here. However, they must be available for the reverse procedure, i.e. for the calculation of the „real“ concentrations from known \( \Delta_r G \) values obtained from tables, estimation methods or gas phase quantum mechanics. Theoretically, \( \Delta_r G \) values from quantum mechanics using continuous solvation models (CSM) must not be corrected with activity coefficients in order to correctly account for the non-ideal behaviour. In practice, the differences between gas and liquid phase are rather small (cf. Chapter 4, in particular Table 4.6), since the solvation effects compensate for both products and reactants.
here I use the unit mol/m$^3$. What do we need to convert the concentrations into the molar fractions? We require the density of the mixture, from which the total amount of material in mol can be calculated by applying the molar mass of the ionic liquid.

However, we do not know the density of the possible liquid membrane phase mixtures (they were not measured in the experiments) nor the partial molar volumes of the species. If the density of the mixture equals the density of the neat ionic liquid (taking into account quasi infinite dilution, where the volume of all solutes is taken as zero), for $K_c$ of 0.2 m$^3$/mol the equilibrium constant $K_a$ equals 906. From this value the Gibbs free energy is -16.88 kJ/mol. The variation of initial concentrations of propylene and carrier results in Gibbs free energies between 16 kJ/mol and -17 kJ/mol. For $K_c$ of 0.1 m$^3$/mol $K_a$ equals 453, for $K_c$ of 0.3 m$^3$/mol $K_a$ equals 1359. For $K_c$ from the simple model of 0.03 m$^3$/mol $K_a$ equals 136. The corresponding values for the Gibbs free energy are -15.16 kJ/mol, -17.88 kJ/mol and -12.17 kJ/mol, respectively. All Gibbs free energy values were calculated at room temperature.

The influence of the density on the equilibrium constant $K_a$ can be considered for the sake of simplicity by the variation of the density of the neat ionic liquid. The results for the realistic range of „mixture” densities are presented in Table 3.16.

<table>
<thead>
<tr>
<th>$\rho$ [kg/m$^3$]</th>
<th>$K_a$ [-]</th>
<th>$\Delta_r G$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>560</td>
<td>-15.69</td>
</tr>
<tr>
<td>1000</td>
<td>680</td>
<td>-16.17</td>
</tr>
<tr>
<td>1250</td>
<td>801</td>
<td>-16.57</td>
</tr>
<tr>
<td>1500</td>
<td>921</td>
<td>-16.92</td>
</tr>
<tr>
<td>1750</td>
<td>1041</td>
<td>-17.22</td>
</tr>
<tr>
<td>2000</td>
<td>1161</td>
<td>-17.49</td>
</tr>
<tr>
<td>2250</td>
<td>1281</td>
<td>-17.74</td>
</tr>
<tr>
<td>2500</td>
<td>1401</td>
<td>-17.96</td>
</tr>
<tr>
<td>2750</td>
<td>1521</td>
<td>-18.16</td>
</tr>
<tr>
<td>3000</td>
<td>1641</td>
<td>-18.35</td>
</tr>
</tbody>
</table>

The variation of the equilibrium constant formulated in terms of concentrations $K_c$ within the limits of optimum facilitation, the variation of initial carrier and permeants concentration and the variation of the mixture density have relatively little impact on the thermodynamic equilibrium constant $K_a$ and on the Gibbs free energy of carrier $\Delta_r G$, which lies between -12 kJ/mol and -18 kJ/mol. For the calculation of reaction enthalpy $\Delta_r H$, entropy term is required. The contribution and change of entropy during reactions in liquids at room temperature is relatively small [103], therefore $\Delta_r S$ can be taken zero. Hence $\Delta_r H$ can be well approximated by $\Delta_r G$. As comparison, optimum $\Delta_r H$ and $\Delta_r G$ values for the optimum facilitated transport were reported to be in the range from -17 kJ/mol and -40 kJ/mol [103].
3. MASS TRANSPORT MODELLING

3.5 Summary

A membrane separation unit using supported liquid membranes for gas/vapour separation has been modelled with respect to isothermal mass transfer. Stationary and transient models for solution-diffusion and for facilitated transport separation in the liquid membrane have been derived. Simulations have been performed, in which parameter variations have been carried out.

Results from the facilitated transport model, which was implemented into the finite elements simulation software Femlab, could be compared to the results obtained by the published analytical model. Although several simplifications and assumptions on

- fluid dynamics (neglecting the Stefan transport),
- solubility and diffusivity data (estimation of absolute values and their temperature dependance, effective diffusivity approach),
- membrane thickness and its porosity (parameters not known exactly),

have been included, the obtained equilibrium constant $K_c$ data, which was the focus of the modelling, have been found to be consistent. In the analytical model, which does not include feed and permeate phase, the optimum equilibrium constant lies at approximately $0.04 \text{ m}^3/\text{mol}$. This value is smaller than the optimum equilibrium constant in the complex model, which was found to be $0.2 \text{ m}^3/\text{mol}$. The difference of an order of magnitude seems reasonable, because in the complex model the feed phase is depleted on the active component along the separation unit and therefore, in order to compensate the permeant depletion, the carrier should be more willing to react with the active component.

The equilibrium constant $K_c$ for the carrier-permeant reaction is formulated in terms of species’ molar concentrations. This formulation is often used in chemistry due to the ease, with which it is obtained in experimental work. In the modelling procedure, this formulation was also used, because it could be more easily implemented in the software Femlab. For the evaluation of thermodynamic properties of the carrier, however, it can not be used directly. It must be converted into the thermodynamic equilibrium constant $K_a$, which is expressed in terms of molar fractions. With a few assumptions on liquid membrane’s physical properties and on the $K_c$ calculated in the mass transport modelling, the desired range of $K_a$ values is derived, whereupon the Gibbs energy change of reaction $\Delta_rG$ and reaction enthalpy $\Delta_rH$ can be calculated. The Gibbs free reaction energy $\Delta_rG$ lies within a range of -12 kJ/mol and -18 kJ/mol. Since the change of entropy in liquid mixtures is small, $\Delta_rH$ can be assumed to correspond approximately to $\Delta_rG$.

With known desired thermodynamic parameters for the carrier-permeant reaction, the main task that remains is the identification of the potential carriers for a chosen gas or vapour separation. Molecular modelling, in particular quantum mechanics methods should, in principle, be able to predict $\Delta_rH$, $\Delta_rG$ and hence $K_a$ for a given carrier-permeant reaction. In the next chapter, molecular modelling methods will be evaluated from the engineering perspective by the treatment of several carrier systems.
4 Molecular Modelling

Quantum chemical calculations together with molecular mechanics and dynamics are increasingly becoming the integral part of chemical, biochemical and engineering research [147, 148]. The major advantage of performing molecular simulations over an experimental approach is the possibility to predict the properties of different compounds or their mixtures [149] before they are synthesised in the lab [150]. Hereby, the experimental risk and research cost may be minimised. This is especially the case in the design of the complex compounds in engineering and in biotechnology [151].

In this chapter it will be shown whether, how and how far the selected methods of molecular modelling, especially of quantum mechanics, are suited for the (in-silico) development of carriers intended to be used in liquid carrier membranes. A short introduction to the methods and the applied software will be given first. Then, some known carriers will be evaluated in respect to their reaction behavior according to the guidelines obtained in the previous chapter. On this basis, an approach for the design of new carriers will be introduced and validated on chosen examples. Hereby, when not noted otherwise, only such compounds should be considered, whose application in the large scale might make sense economically. Too exotic syntheses will, of course, be prohibitive to follow this credo. Subsequently, some sample state-of-the-art calculations from the field of gas-liquid thermodynamics based on quantum mechanics will be discussed. In one example, molecular dynamics will be used for the determination of (self-)diffusion coefficients of chosen components in the particular ionic liquid used in a carrier membrane from both mass transport modelling and the experimental chapter.

4.1 Introductory remark

Adolphe Quetelet (1796-1874) said: „The more progress physical sciences make, the more they tend to enter the domain of mathematics, which is a kind of center to which they all converge. We may even judge the degree of perfection to which a science has arrived by the facility with which it may be submitted to calculation.”

Availability of fast personal computers, access to high-end clusters and user-friendly software enables even a main-stream chemist or an engineer to bring - at least theoretically - a considerable part of the chemistry and chemical thermodynamics to his or her desktop. Due to the ease at which routine chemical computations can be performed today, the danger that „...many people don’t understand even the most basic description of how the calculation is done and are therefore successfully doing a lot of work which is, frankly, garbage...“ [152] is not insubstantial.
In order to save time and money, one should keep in mind that today, computational chemistry is a fully developed research field on its own and that a really profound work in this field should be left to a full-time employed or prospective specialist.

4.1.1 Software

Apart from the problem of choosing the right (commercial or non-commercial) software packages - for only the right tools or even combination of them might do the right thing - one is faced with many computational options at even more striking abundance of different levels of theory. Having in mind industrial engineering problems, quick and reliable methods within reasonable accuracy are required. But these are still not fully available and find themselves under development [153]. Semi-empirical (SE) and density functional theory (DFT) methods are currently the most widely used approaches for tackling industrially relevant tasks [154]. Covering this demand, in some all-in-one software packages, exclusively SE and DFT programs are included. They completely renounce all ab-initio methods, which should be used as a more conservative reference when the results calculated by DFT are doubtful or found not to be reliable enough.

Interestingly, although general computational techniques have the same theoretical basis (starting from e.g. LCAO, linear combination of atomic orbitals, concept), only ab-initio Hartree-Fock (HF) and Møller-Plesset (MP) methods supposedly [155] give exactly the same results regardless of which software package is used. My own experience after extensive software testing of several quantum mechanical codes has shown that the results from some ab-initio and all DFT calculations can only be compared within the same software. Thus, the choice of the software does matter. Considering the speed of calculations, the accuracy (which remains questionable without experiments) and comfortability of handling, I have decided to use the combination of the commercial programs Spartan [156], Gaussian [157], Turbomole [158] and Materials Studio’s DMol 3 [159]. Furthermore, very good codes of Hyperchem [160], ADF [161] and GAMESS(US) [162] were tested, but not used any further. Many more attractive codes with outstanding features are available [163], but their evaluation would break the limits of this work.

Semiempirical programs like AMPAC [164] or MOPAC [165] or programs based on molecular mechanics like MOE [166] cannot be used for accurate calculation of carrier properties for facilitated transport membranes. They can, however, play an essential role as preoptimisation tools prerequisite to quantum mechanics. Semiempirical routines from Spartan, however, proved to be sufficient for the treatment of all problems encountered.

The state-of-the-art program COSMOtherm [114], where results from quantum mechanical calculations are required in order to perform statistical thermodynamics, was used for the prediction of thermophysical data of chosen liquids. For molecular dynamics simulation, the program GROMACS [167] was tested. However, for convenience of handling, Materials Studio’s Discover [159] was used for production runs.
4.1. INTRODUCTORY REMARK

4.1.2 General procedures in molecular modelling

The first information on the molecular systems of interest is usually obtained from the literature. When some basic physico-chemical principles of the system - not necessarily all the mechanisms in detail - are known, one can use intuition to variate the known structures and thus develop new molecular systems, whose properties might be more suitable for the focused application. General scheme for such target oriented conduction of molecular modelling simulations is given in Fig. 4.1. This approach is consequently applied in almost all examples treated in this work.

Figure 4.1: Principal flow sheet for molecular modelling

Firstly, knowing the molecular system means to abstract the structural information of all species involved in the system and to generate appropriate inputs. Structures can be, for example, derived from the X-ray diffraction and spectroscopical experiments (e.g. IR) or mass spectroscopy, NMR etc. Then, one has to decide whether to calculate the transport properties within a molecular ensemble ending with diffusion coefficients or to focus on thermodynamics and kinetics.

In the general scheme presented above, two fields can be distinguished. The first field represents the force field based methods: molecular mechanics (MM) and molecular dynamics (MD). Force field methods are widely used for conformational analysis and for study of many-particles motion on molecular level\(^1\). Quantum mechanics, which is based on mathematical routines that approximately solve Schrödinger equation, is the second field. Quantum mechanics calculations are used for the determination of thermodynamics and under favourable circumstances also for kinetics. Hereby, gas phase can be treated routinely. For liquid systems, several modelling approaches exist, all of them being not trivial. Approximate solubilities of solids and liquids, Henry coefficients and activity

\(^1\)Force field methods can cope with the systems composed of very large number of atoms. For example, water transport through biological membranes, composed of more than 100000 atoms could be studied with EGO [168] and NAMD [169].
coefficients can be efficiently obtained by COSMOTHERM method for the most chemical systems. For more detailed information on individual steps concerning quantum mechanics in the scheme above, Appendix B should be consulted.

Quantum mechanics is today already coupled with dynamics simulation [170], first attempts dating back some 20 years. This domain is however, still in the stage of university research and the respective tools are not used in this thesis.

4.2 Known Carriers

In order to correlate the properties of known carriers to those of potential ones, one has to evaluate carriers already used in carrier membranes or related processes first. In the published literature, such projects are hardly encountered [171] and one is actually on his own.

It is reasonable to assume that each newly developed carrier will have to share some essential properties with known ones. The common features concern especially the reaction enthalpy, activation energy and the course of energy path as well as the spontaneity of the carrier reaction with the desired compound.

In the following sections, if not stated otherwise, general reaction of the type:

\[ \text{carrier} + \text{desired permeand} \leftrightarrow \text{adduct} \]

is considered, where the thermodynamics is accounted for from the left (reactants) to the right (products) side of the equation.

**Focused applications**

In the focus of this thesis are in particular carriers for the membrane systems that concern:

- separation of oxygen from nitrogen and
- separation of alkenes from alkanes, especially of ethylene and propylene from ethane and propane, respectively.

Carriers for removal of acid gases (CO$_2$, SO$_2$, H$_2$S), primarily CO$_2$ from e.g. natural gas (CH$_4$, H$_2$), carriers for carbon monoxide, hydrogen and water vapor are also shortly mentioned in this context.

4.2.1 Carriers for Oxygen

Known carriers for oxygen are often also used as oxidation catalysts (e.g. [172, 173, 174, 175]). One can therefore find excellent compilations of several potential carriers/catalysts in organic synthesis monographs, which focus on selective oxidation reactions [176].
4.2. KNOWN CARRIERS

Since reversible binding and transport of oxygen is crucial to all aerobic living beings, this field was long a subject of different investigations, especially those revealing phenomena from the standpoint of biomimetics. The work in this field was thoroughly reviewed [177, 178, 179], but did not provide any useful facts for extending the knowledge towards a technical application.

Oxygen Carriers from the Co-Salene Family

The simplest carrier for oxygen that is easily synthesised (see Appendix C.1), is bis-(N,N'-disalicylalethylendiamin)-µ-aquocobalt, shortly Co-Salen. This compound was used during the second world war by American military for oxygen production by means of pressure swing absorption (PSA) [75]. Several deviations of this compound were already focused at that time [180]. Until recently, Co-Salen and some related compounds have also been used as carriers in membrane separations [181, 182, 183]. From the variety of available carriers, compounds shown in Fig. 4.2 are treated quantum mechanically in this work. All these carriers are radicals (compounds with one unpaired electron) and act as the traps for oxygen, whose stablest form at ambient conditions is actually a biradical (compound with two unpaired electrons). The constellation at which oxygen is attached to the carrier is called superoxo arrangement.

![Co(3-R Salen) Co(3-MeOsaltmen) Co(n-prdpr)](image)

Figure 4.2: Selected oxygen carriers from Co-Salen family: a) Co-Salen b) Co-Saltmen ("Baker") c) Co-Salen-pdpta (R₁=-H, -F, -NO₂, -OCH₃; R₂=water, ammonia, imidazole, pyridine, DMAP)

In order to find the global energy minima required for evaluation of thermochemistry of the above compounds, firstly, systematical rotational analysis for the determination of the oxygen position is conducted on PM3 and DFT (DMol³, BLYP, DNP, AER core treatment) levels. The results for the internal rotation of oxygen expressed by the torsion angle in Co-Salen are shown in Fig. 4.3.

One can see on the example of Co-Salen, that semiempirical PM3 calculations² reflect the results of more precise DFT calculations in this case very well. All calculations yield four distinctive minima within the rotational potential surface. The profiles do not

²PM3 method was originally restricted to elements also parameterised in AM1 method. In Spartan quantum chemical program, in its semiempirical routine, however, almost all transition metals are included in the parameterisation, making this tool very valuable for a wide variety of compounds.
Figure 4.3: Determination of the oxygen position in the oxygenated Co-Salen through constrained internal rotation search: a) a comparison of DFT and PM3 calculations (go=geometry optimisation; sp=single point). b) The numbers on the atoms denote the torsion angle used as the coordinate on the potential energy surface.

completely fit to each other due to the additional internal barrier (approx. 11.8 kJ/mol) of the bridging ethylene group, which topples over in PM3 calculation and does not change in DFT calculation. In DFT calculation, the barrier seems to be too high for this conformational change. As a rule of thumb, reactions with barriers below 20 kJ/mol will take place spontaneously at ambient conditions. Therefore, oxygen rotates and spins around its bond with cobalt almost freely, i.e. with or without positional change of the ethylene bridge that also takes place simultaneously.

Four subsequent full geometry optimisations with DFT, starting at torsion angle of 40, 130, 220 and 330 degrees without any constraints are necessary in order to reveal the real global minimum which lies at 223.36 (-136.64) degrees. The energy of this global minimum is yet another 5.28 kJ/mol lower than the lowest energy of the conformer found by constrained calculation. Once having found the final geometry, the oxygen molecule is removed from the compound. Subsequently, both oxygen (triplet in the ground state) and deoxygenated carrier (doublet in the ground state) are submitted to optimisation at the same DFT level. The reaction enthalpy at 0 K without zero point and thermal corrections is found to be -76.15 kJ/mol.

In further calculations (this was also revealed in the experiments) it is found that axial base is required in order to achieve the convergence in the (numerical) vibrational analysis that is needed for the full evaluation of thermochemistry. Proximal and distal bases are, as known from the investigations of biological systems, ligands that stabilise and influence the reactivity of the central (here five-coordinated) metal ion. Unfortunately, through the presence of these bases - water, pyrimidine, imidazole and some related compounds have been considered - the number of atoms in the molecule increases and additional internal rotations arise that also have to be accounted for. Once oxygen minimum is found, the relative position of the proximal bases must also be determined. The same constrained type of calculation as in the case of oxygen must be performed. As an example, the results for the constrained rotation of imidazole and pyridine in Co-Fluomine are shown.
4.2. KNOWN CARRIERS

in Fig. 4.4.

Figure 4.4: Determination of the positions of the proximal bases imidazole and pyridine in Co-Fluomine: a) a comparison of DFT and PM3 calculations b) molecular structure and torsion angle as reaction path

PM3 method again proves to be a good choice as a prerequisite method for subsequent geometry optimisations at higher levels of theory. Therefore, the procedure described above is repeated for the compounds Co-Salen, Co-Fluomine, Co-Nitromine and Co-MetOmine using pyridine, imidazole, ammonia and water as proximal basis. The results based on minimised structures for enthalpy at 0 K without thermal corrections are gathered in Tab. 4.1. Calculations referring to Co-Nitromine compound in its carrier and in its oxygen adduct form do not converge (n.c.) with ammonia and water as proximal bases under any circumstances, i.e. under any starting geometry. The cause for this seems to be the high steric penalty caused by the adjacent NO$_2$ groups that results in strangely twisted carrier molecule.

Table 4.1: Reaction enthalpies for oxygen caption using different proximal bases in selected carriers (Turbomole, BP, def-TZVP; without zero correction)

<table>
<thead>
<tr>
<th>group</th>
<th>Pyridine</th>
<th>Imidazole</th>
<th>Ammonia</th>
<th>Water</th>
<th>no base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-Fluomine</td>
<td>-49,51</td>
<td>-54,88</td>
<td>-56,66</td>
<td>-53,79</td>
<td>-26,03</td>
</tr>
<tr>
<td>Co-Nitromine</td>
<td>-43,68</td>
<td>-53,76</td>
<td>n.c.</td>
<td>n.c.</td>
<td>-23,60</td>
</tr>
<tr>
<td>Co-MetOmine</td>
<td>-51,66</td>
<td>-57,78</td>
<td>-59,81</td>
<td>-56,46</td>
<td>-26,86</td>
</tr>
</tbody>
</table>

The reaction enthalpy for the carrier - oxygen reaction lies in the same energy window for all calculations and does not crucially depend on the type of the proximal base. However, it is significantly more negative than in cases, where no base is used at all. For comparison, experimental values for enthalpies of the above reactions lie around -80 kJ/mol.

Experimentally it was found that the best performance in membrane applications is achieved by the usage of the proximal base 4-dimethylaminopyridine (DMAP). With BP (GGA) functionals using DFT optimised semi-core pseudopotentials and DNP basis set
in DMol³, the reaction enthalpy of -69.90 kJ/mol is obtained for this so called "Baker"-compound (Fig. 4.2b. Analogous calculation in Turbomole with def-TZVP basis yielded -52.76 kJ/mol, respectively. This finding does not confirm that this compound would stand out from the other pyridine based compounds.

The compound Co-Salen-pdpta has a very unusual non-planar structure shown in the Fig. 4.5a. This structure is caused by the free electron pairs of the two nitrogen atoms constituting strained bridging chain, also acting as a proximal base with it amino function in the middle. The main advantage of this compound over the planar ones is the possibility of prevention of the dimerisation of the carrier/adduct molecules: the carrier and the oxygenated adduct are both doublets and therefore radicals. These are prone to irreversible combination to singlet products without (Fig. 4.5b and with oxygen bridge (Fig. 4.5c. Bridged products are almost inactive in respect to further oxygen uptake. This is experimentally confirmed.

![Figure 4.5: Structures of: a) oxygenated Co-Salen-pdpta (not a minimum in respect to oxygen) b) Co-Salen dimer c) Co-Salen oxygen bridged dimer](image)

In DMol³ and Turbomole calculations with BP (GGA) functionals using DFT optimised semi-core pseudopotentials and DNP basis set on the one hand and def-TZVP basis set and RI-approximation on the other hand, the Co-Salen-pdpta-oxygen reaction enthalpies of -96.07 kJ/mol and -81.63 kJ/mol are obtained.

Interestingly, so far numerical basis sets have shown systematic deviation to higher negative enthalpies (more exothermic reactions) when compared to Gaussian basis sets. In this particular case, DMol³ reproduces experimental values better than Turbomole. Nevertheless, one have to keep in mind that the values obtained are not corrected for finite temperatures and that thermal corrections further lower the enthalpy.

**Transition state (TS) search** In the course of TS search, the first question in the treatment of this particular caption reaction type to be answered is, in what multiplicity arrangement does triplet oxygen attach to the doublet carrier molecule. In the case of Co-Fluomine-Pyridine - oxygen reaction (CFP), here taken as an example, both, doublet and quartet options are considered at the whole reaction path. The following calculations are performed with DMol³ GGA BP functional, importantly, all of them in corresponding unrestricted shell configurations. The core is treated with DFT-SCP. For scanning potential surfaces, DND basis set with SCF convergence level $10^{-5}$ hartree is used. More
4.2. KNOWN CARRIERS

accurate options for thermodynamics were afterwards set to DNP basis set and SCF convergence level $10^{-6}$ hartree.

The results of the direct usage of LST (linear synchronous transit) method to locate TS for these two multiplicity options are shown in Fig. 4.6a. As expected, the quartet energy increases with decreasing reaction path, defined as the distance between the core metal and the (nearer) oxygen atom. This rules out the quartet option at least in the vicinity of energy minimum, which is clearly a doublet (Fig. 4.6b). In reactions where multiplicity change takes place at the very transition state, the direct simple application of LST or QST (quadratic synchronous transit) searches can not be successful. (One might, of course, adjust the multiplicity as this was done here, but in a single calculation, both multiplicities are not allowed. One has to decide, which occupational numbers are to be used.) This is also true for all similar searches, where intermediate structures between reactants and product(s) resembling transition state are given as input. The transition state search on the same system in Gaussian program with proposed transition structure also led to no results. In our particular case, I decided to postulate (and this can be reasonably postulated) that the true transition state is located where the doublet and quartet energies cross, i.e. posses the same value. However, for this, more detailed mapping is required. Therefore, more points on reaction coordinate had been (re)calculated. These are shown in detail in Fig. 4.6c. Indeed, one can locate an energy barrier, denoted as $E_A$: the energy reference point is taken to be the reactants at (ideally) infinite distance from each other (far right in the diagram).

---

Figure 4.6: Transition state search in Co-Fluomine - oxygen reaction: a) LST (single point energy) scans b) details near equilibrium position c) details near doublet-quartet energy crossing (estimated activation energy: 3.02 kJ/mol) d) superimposed doublet and quartet structure minima as obtained from DMol³.
If the energies of the individual triplet oxygen and the individual doublet carrier molecules are taken as reactants (which is usually done for isolated molecules at infinite distance) and the energy of the non-defined multiplicity state at the energy crossing is calculated, the activation energy $E_A$ for this reaction lies between 9.79 kJ/mol (for doublet) and 2.37 kJ/mol (for quartet) at 2.814 Å. Interestingly and even more importantly however, neither imaginary frequencies nor approximate detachment normal modes can be found at this geometry with the computational method applied.

The activation energy that is automatically calculated by the DMol$^3$ program at 4.341 Å is even much greater (19.80 kJ/mol, with two imaginary frequencies $\omega=-75$ cm$^{-1}$ and $\omega=-87$ cm$^{-1}$), but is - as a doublet at such bond distance - a physical nonsense. Quartet calculation at the same initial geometry did repeatedly not converge.

The bonding nature of the oxygen to the central metal ion can also be visualised (cf. Fig. 4.7) by the total electron density at 0.0002 electrons per Bohr$^3$ and at 0.2 electrons per Bohr$^3$. The former density represents the interaction surface at distances that are about 10 orders of magnitude greater than those of corresponding van der Waals radii, the latter corresponds approximately to the covalent bond densities. The picture of the electron density does scarcely depend on the multiplicity choice. Therefore, it can be stated that the true transition state is indeed located at 2.814 Å, since at the 4.341 Å no electron interactions can be observed (two closed surfaces). According to the repeated single point calculation with Turbomole, which did not converge for 3 unpaired electrons, TS confirms a doublet: geometry optimisation from TS results in the adduct. It should be noted further, that at the distance of 4.341 Å non-constrained minimisation calculation switched to doublet does converge but does not yield the expected adduct: it only forces singlet oxygen! The reactants are too far away to properly interact in order to yield the adduct.

Figure 4.7: Electron density isosurfaces and the comparison to the vdW surfaces for potential transition state structures of Co-Flumine - oxygen reaction a) oxygen still attached at 2.814 Å b) oxygen detached 4.3 Å. Inner isosurfaces correspond to covalent bond densities.
4.2. KNOWN CARRIERS

Another important finding based on visualisation from Fig. 4.7 is the nature of oxygen interaction with the metal site. Electron density surfaces within the outer electron surfaces correspond approximately to bond densities. It can be concluded that the interaction of both oxygen and proximal base pyridine is of non-covalent but rather of typical ligand-like coordinative character.

Before the subject of kinetics is turned to, two further issues must also be discussed. The drop in the doublet energy of the adduct between 4,8 and 5,4 Å below the energy of the quartet is a non-sense result. The QM treatment of dioxygen seems not to be sufficiently accurate for this non-typical molecular system of two quite independent molecules, where the wave function stretches itself beyond the usual bond lengths. Although all bond interactions are still within the orbital cut-off distance (two times 4 Å), at 4,8 Å singlet oxygen suddenly becomes more stable than triplet oxygen and in this way contributes to overall lower energy. This can, due to the paramagnetism encountered in „real” oxygen, clearly not be the case.

The fine resolution of the energy around the equilibrium position (1,909 Å) surprisingly gives a relatively constant energy plateau, i.e. calculation readily converge for several distances within the narrow distance window. This implies that the compound is stable at more than one or at not so „stiff” or restricted geometries. Energy fluctuations between 1,9208 and 1,9600 Å appear as the apparent detachment point of oxygen (Fig. 4.6b), however, further increase of the distance leads again to lower energies, rejecting this hypothesis.

However, all these findings may depend on the specific orbital or other particular implementation in the software. After having located and postulated the possible transition state geometry as well as other geometries involved in the reaction with DMol³, these structural data is used as an input for treatment with Turbomole. For convenience with respect to time/benefit, computationally cheaper BP(RI)/SV(P) level and default settings were used for the structure calculation. Firstly, single point energies only and subsequently new energy minima were calculated. A geometry optimisation was performed on postulated transition state, whereas the distance of core metal to the nearer oxygen was constrained to 2,814 Å. Other Co-Fluomine structures were fully optimised without restrictions. Subsequent vibrational analysis yields the zero point energy for each compound.

Here, it is of extreme importance to notice that - in contrast to the all calculations by DMol³ above - only one and single imaginary frequency exactly corresponding to a transition state vibrational mode was identified in two independent subsequent runs (ω₁=-86,04 cm⁻¹ and ω₁=-85,72 cm⁻¹)³.

The overall energetics as obtained by Turbomole at different stages of the calculations reads as follows: reaction enthalpy based on electronic energy for single point calculation on DMol³ geometries yields -70,6 kJ/mol and +0,7 kJ/mol activation energy (with 4 imaginary frequencies). The subsequent optimised run gives -71,3 kJ/mol and -21,06 kJ/mol activation energy (1 imaginary frequency). Applying the corrections for the zero point, the reaction enthalpy is reduced to ΔH = -63,9 kJ/mol and activation energy to -18,5 kJ/mol.

³In theoretician’s slang the finding of the transition state is „the reason to celebrate”!
Finally, when I correct these values for finite temperature of 298.15 K and 10^5 Pa, I get \( \Delta H = -65.9 \text{ kJ/mol} \) and activation energy to -19.4 kJ/mol (which are the values we will use in subsequent considerations).

In Turbomole thus we obtain clear behaviour of the transition state, but also perplexing negative activation energy (-19.4 kJ/mol), which is hard to interpret. On the one hand, this behavior may typically be attributed to loose transition states, on the other hand computation technique might not be sensitive enough to reveal the multiplicity effects\(^4\).

The next question is: “How fast is this reaction?” Due to the lack of all the information on distinctive and unambiguous transition state, strict application of transition state theory is nor reasonable nor straightforward and in this case, an expert should be consulted. Classically, for the calculation of the reaction rates, the fundamental equation of transition state theory, the so called Eyring equation is applied:

\[
k = \frac{k_B T}{h} \frac{q_{\text{tot,TS}}^i}{q_{\text{tot,cARRIER}} q_{\text{tot,oXYGEN}}} e^{-\frac{E_A}{RT}},
\]

where \( k_B \), \( T \), \( h_P \), \( q_{\text{tot,i}} \), \( E_A \) and \( R \) represent Boltzmann constant [J/K (and per molecule)], temperature [K], Planck constant [Js], total partition function of the respective species \( i \) [m^-3], activation energy of reaction [kJ/mol] and universal gas constant [J/mol K], respectively. Consequently, the unit of the reaction rate constant \( k \) is [m^3/(s molecule)] and must be multiplied by Avogardo’s number [molecules/mol] in order to obtain second order reaction rate [m^3/s mol].

Indeed, we can use this equation to the certain level. The required quantities to be plugged into this equation can be obtained from the output file of the Turbomole’s freeh (free enthalpy) subroutine. The electronic data of the calculation, thermal corrections for enthalpy, contribution of entropy and values for the product of partition functions\(^5\) \( \ln q_{\text{tot}} \) of all the compounds involved at 298,15 K and 1 bar are given in Tab. 4.2. Having the values of enthalpy and entropy, we can also calculate the Gibbs free enthalpy of reaction, the discussion of which will be performed later with more suitable compound.

Now, there are two possibilities of further treatment: activation energy can be either used as it is (I) or it can be set to zero (II). Reaction rates (second order reaction) resulting from both considerations yield \( k_I = 1.259 \cdot 10^8 \) m^3/s mol and \( k_{II} = 4.953 \cdot 10^4 \) m^3/s mol. In the latter, more reasonable case, the rate constant equals the frequency factor \( k_\infty \).

Negative activation energy formally increases the rate of reaction. Although the numbers obtained by this procedure are exorbitantly high, the consequence of these results (not necessarily the numbers) have practical importance for e.g. the mass transport modelling. It can be stated that this kind of reaction is instantaneous and that it must be wholly

\(^4\)See the discussion of the wavefunction stability in [184]. Furthermore, refer to [127], where the calculation of reaction rates for barrierless reactions is shortly treated by different theories.

\(^5\)Partition function has the same meaning in statistical thermodynamics as the wavefunction has in quantum mechanics. In Gaussian program, the values for partition functions are more accurately printed out than in Turbomole, but natural logarithm usually sufficiently accurately reproduces their values. Mind that translational partition function depends on temperature and pressure. When it is (as usually is) given in „per volume of single molecule of ideal gas at given T and p“, one has to multiply the output value from Turbomole or Gaussian by factor \( \frac{p}{k_B T} \). Please note also that \( q_{\text{tot}} = \prod q_i \) and \( \ln q_{\text{tot}} = \sum \ln q_i \).
4.2. KNOWN CARRIERS

Table 4.2: Electronic energies, zero point vibrational energies, thermal corrections for 298.15 K and 1 bar and total partition function for CFP-O_2 system

<table>
<thead>
<tr>
<th>Carrier</th>
<th>Energy [Ha]</th>
<th>ZPVE [kJ/mol]</th>
<th>H_{corr} [kJ/mol]</th>
<th>S_{tot} [kJ/molK]</th>
<th>q_{tot} [1/m^3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier</td>
<td>-2706.887393378</td>
<td>793.5</td>
<td>867.509</td>
<td>0.75762</td>
<td>9.97802·10^{31}</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-150.2260793394</td>
<td>8.562</td>
<td>17.2589</td>
<td>0.20203</td>
<td>2.59693·10^{34}</td>
</tr>
<tr>
<td>Adduct</td>
<td>-2857.140624777</td>
<td>809.4</td>
<td>890.149</td>
<td>0.80398</td>
<td>1.70781·10^{53}</td>
</tr>
<tr>
<td>TS</td>
<td>-2857.121497152</td>
<td>804.6</td>
<td>886.399</td>
<td>0.83230</td>
<td>3.43024·10^{54}</td>
</tr>
</tbody>
</table>

governed by diffusion process within the process phase (liquid, ionic liquid, polymer, etc.). Exactly this approach was correctly applied in the Chapter 3.

Furthermore, with no barrier present, the extent of the sorption for the isolated gas phase is thermodynamically unambiguous and seems to be not dependant on intrinsic reaction kinetics. The construction of ideal adsorption isotherms in term of equilibrium constant of reaction is possible but unfortunately not reasonable. Primarily, this is due to the inaccuracy of computed results for both the enthalpy and/or the free Gibbs enthalpy when compared to the measurements. Let me explain this behavior theoretically on an imaginary example. Let be species i in equilibrium with species j, i \rightleftharpoons j. The equilibrium constant K may be defined as:

$$K = \frac{n_j}{n_i} = \frac{k_i}{k_j} = e^{\frac{\Delta E_0}{RT}}$$

where the first term is simply the mol ratio between the species, the second term are the reaction rates, given here for the sake of completeness. The difference between energy states $E_j - E_i$ is denoted with $\Delta E_0$. Let us assume that true value for $\Delta E_0$ is e.g. -8.75 kJ/mol. At 300 K calculated equilibrium constant is 33.39. Let us now determine $\Delta E_0$ in an imaginary calculation experiments and let us obtain values for $\Delta E_0$ that slightly deviate from the „true” value. In Fig. 4.8a one sees the dependance of equilibrium constant on the temperature and on the deviation from the correct $\Delta E_0$ value. Even more interesting is the behaviour at the constant temperature (300 K), where different true values for $\Delta E_0$ are assumed.

Equilibrium constant strongly depends on even the smallest deviations from the true value of $\Delta E_0$, whereas the deviations tend to increase for increasing $\Delta E_0$ values (Fig. 4.8b). A difference in $\Delta E_0$ of more than 1 kJ/mol proves to be prohibitive even for qualitative evaluation.

Since the values from DFT deviate up to 20 kJ/mol from the experimental values, one should at this point abandon any further discussion on theoretical construction of sorption isotherms. On the other hand, one can understand the very endeavours of the theoretical chemists to determine the exact energies of the individual compounds. For achieving

---

6I have used here simplified Boltzmann statistics, which does not take partition functions into account. This representation illustrates the problem well enough. However, we will encounter the complete treatment of equilibrium from the point of view of statistical thermodynamics later in this chapter.
Figure 4.8: Dependence of thermodynamic equilibrium constant $K$ with respect to the exact determination of the system (reaction) energetics a) temperature variation b) energy level variation

this, an extremely good approximate solution of Schrödinger equation is necessary. For industrially relevant chemicals, this is hardly possible [148]. A work around might be considered to be so called „compound chemistry” methods (cf. [184]), which however, fail for compounds of more than 40 atoms even on big parallelised cluster computers, especially if those contain transition metal atoms, for which there exist no appropriate basis sets (only elements up to argon can be treated).

Dicobalt Oxygen Carrier

As mentioned above, doublet carriers activate oxygen and promote autooxidation. This is the main reason for the deactivation of Co-Salen related compounds to take place. In contrast to these very reactive doublet monocobalt dioxygen complexes, it might be more reasonable to use such a compound that would react with triplet oxygen in order to produce a singlet product. Indeed, oxygen bridged compounds that fulfill this criteria were reported and partly characterised [185]. Although not easy to synthesise, another compound [186] that might find the potential use in membrane separations is shown in Fig. 4.9. As the mayor advantage of this carrier over monocobalt carriers, comparably small degradation to inert form was observed.

Due to the flexible cage of the compound, conformational analysis on MM (with MMFF force field in Spartan) level is performed on partially fixed geometry around both metal centres. Cobalt ions are stabilised in the „crypt” by coordination with amino groups. Refinement of the structure with PM3 method results in the strange hydrogen bonding of hydroxy group and does not yield any good initial guess as input for DFT calculation. Therefore, some minor manual adjustment are required.

All DFT calculations, even singlets, are performed as being unrestricted open-shell systems. Only this constellation allows the realistic assessment of results\(^7\). With BP/DNP

\(^7\)As an example, an open-shell singlet oxygen has different energy than a closed-shell singlet oxygen!
and DFT-SCP core treatment, the reaction enthalpy for oxygen caption of -169.5 kJ/mol is obtained. This is approximately two to three times as much as in the cases above. This is not unreasonable: in the course of reaction, two new coordination bonds are formed and all the electrons are now paired. Transition state for this reaction was not found by any method or approach.

Furthermore, such high negative reaction enthalpy is indeed desirable: it enables more control over the adsorption equilibrium position in the range of technical relevant temperatures. In cases, where the reaction enthalpy is too low, adduct can only be built at low temperatures, this being a notorious problem with all carrier systems. Lower temperatures also automatically lead to smaller diffusion coefficients and prevent overcoming the kinetic barrier, if applicable.

**Some Other Oxygen Carriers Based on Cobalt**

More recently, compounds based on polypyridine were reported [187] that show half-life time of 8 months in a non-aqueous environments. It must be noted that these carriers resemble much the Co-Salen in that they have only one central metal atom. In the course of reaction with oxygen, two metal center adduct is built, which dissociates at enhanced oxygen partial pressure. Another compound reported by the same research group [188] is the family of the solid state cyanocobaltates. The advantage for the use of these two groups in the (hopefully low coordinating) ionic liquids might be their ionic character, in order to promote solubility. No computational study was performed on these compounds.

**Iridium Carrier for Oxygen**

Chlorocarbonyl-bis(triphenylphosphine)iridium, so called „Vasca’s compound“ was firstly reported as an oxygen carrier in 1963 [189]. In spite of the reported slower oxygenation

This is true in spite of formally equal orbital occupancy.
rate compared to known carriers at that time, the compound has drawn much attention to scientific community, mainly due to the unusual triangular peroxo metal-dioxygen geometry, where the kind of bonding mode was heavily discussed. Extensive x-ray studies [190, 191] and, later on, simulations with \textit{ab-initio} methods have been performed on closely related analogous compounds [192].

Although a lot of work, particularly in the field of selective oxidation catalysis, has been devoted to the carrier/catalyst, the reaction enthalpy for oxygen caption is still knot known today. To my best knowledge, it has not been determined either experimentally or with computational methods. The mechanism of reaction, especially the way how oxygen approaches the active site of the carrier is also not known. Here, I attempt to determine the missing data. A first glance at the molecular system reveals that proper computational treatment of this carrier must turn out to be a real challenge.

For evaluation of thermochemistry, firstly, conformational analysis for locating the global energy minima of educt and product is focused - just in the same way as this was performed in the case of Co-Salen oxygen carrier above. In this case, internal rotation of both triphenylphosphine groups relative to each other and the internal rotations of phenyl groups around their C-P bonds play a great role, whereas the latter constellations are simply the result of the former. Furthermore, considering the postulated reaction path, reactants, if they are smoothly to be converted into the products, must undergo only small energetic changes in conformation.

Experiments have shown that a solid compound does not react spontaneously with oxygen but does so when it is dissolved in benzene at room temperature. Firstly, this implies certain rotational degrees of freedom of both triphenylphosphine groups in a solution and negative free Gibbs energy for solution only. The reaction enthalpy must therefore compensate the energy penalty arising from eventually unfavoured product geometry. Secondly, since benzene was used as the solvent in experiments, quantum mechanics treatment should be performed in the gas phase first and then in the liquid phase.

Semiempirical and DFT evaluation of the educt give quite different relative rotational position of the two triphenylphosphine groups. In SE calculation, both groups are completely staggered ($\theta \approx 180$ degrees), whereas DFT results seem to account for the intramolecular $\pi$-interactions of all the phenyl groups. Rotational analysis of the gas phase geometries for both educt and product is given in Fig. 4.10.

The relative positions of ligands other than $\text{P(Ph)}_3$ are not considered. It can be seen clearly that three distinctive minima exist on both potential energy surfaces. Interestingly, in case of product, rotational barriers appear more balanced, probably due to the presence of oxygen, which “smooths” the PES (potential energy surface).

Starting at each potential minimum, and comparing the obtained geometries with X-ray studies of the product, a consensus can be found on the geometries of the reactants and products. The structures are shown in Fig. 4.11, where atoms for constrained $\theta$ rotational analysis performed above are also denoted.

Now, having the approximate geometries, it is possible to conduct more accurate energy calculations. All gas phase optimisations converge without problems on DFT level, resulting in consistent and well comparable geometries. The results of the treatment with
different software codes and methods are compiled in Tab. 4.3. All data hold for standard conditions, i.e. at 298.15 K and 1 bar. Thermal corrections were performed and applied throughout. Tomasi’s polarised continuum model (PCM) and its isodensity variant (IPCM) were tried to be performed, where the relative permittivity of the solvent in the calculation study was set to $\epsilon=2.28$. Reasonable solutions for their inclusion into total energy could not be found by any solvation model or any software. Turbomole yielded minimised structures, however, minima confirmation by vibrational analysis resulted in more than 5 imaginary frequencies for both educt and product in many attempts. Results were discarded (disc.) here as well as in Gaussian/IPCM, where the calculation of energy did not converge.

*Transition state search by attempt of the computational costs reduction* Important for understanding the mechanism of reaction are the observations from the performed x-
Table 4.3: Vasca complex and reaction thermodynamics acquired with different computational approaches (AER, all electron relativistic; ECP, effective core potentials; SCP, semi core potentials)

<table>
<thead>
<tr>
<th>software</th>
<th>functional</th>
<th>basis set</th>
<th>core treatment</th>
<th>settings</th>
<th>$\Delta H_{\text{tot}}$ [kJ/mol]</th>
<th>$\Delta G_{\text{tot}}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMol3</td>
<td>BLYP</td>
<td>DNP</td>
<td>AER</td>
<td>smear</td>
<td>-58.78</td>
<td>-7.51</td>
</tr>
<tr>
<td>DMol3</td>
<td>BP</td>
<td>DNP</td>
<td>ECP</td>
<td>no smear</td>
<td>-64.69</td>
<td>-13.48</td>
</tr>
<tr>
<td>Gaussian</td>
<td>B3LYP</td>
<td>6-31G(d)</td>
<td>LANL2DZ (Ir)</td>
<td>no smear</td>
<td>-57.28</td>
<td>-6.17</td>
</tr>
<tr>
<td>Gaussian</td>
<td>B3LYP</td>
<td>6-31G(d)</td>
<td>LANL2DZ (Ir)</td>
<td>IPCM</td>
<td>-3.76</td>
<td>47.69</td>
</tr>
<tr>
<td>Spartan</td>
<td>B3LYP</td>
<td>6-31G(*)</td>
<td>LACVP(*) (Ir)</td>
<td>disc.</td>
<td>-13.40</td>
<td>25.04</td>
</tr>
<tr>
<td>Turbomole</td>
<td>BP</td>
<td>def-TZVP</td>
<td>ECP (Ir)</td>
<td>RI</td>
<td>-3.07</td>
<td>41.84</td>
</tr>
<tr>
<td>Turbomole</td>
<td>BP</td>
<td>def-TZVP</td>
<td>ECP (Ir)</td>
<td>RI, PCM</td>
<td>disc.</td>
<td>disc.</td>
</tr>
</tbody>
</table>

Ray studies, where it was found that carbonyl and chlorine ligands are indistinguishable. When the approach of oxygen can happen only from one side, the two groups would be distinguishable. This observation rules out the hypothesis of the carrier to be considered in triplet ground state. It could be confirmed computationally that carbonyl and chlorine ligands in triplet ground state do not stretch linearly as displayed in Fig. 4.11a but remain at angle during minimisation. The calculation for transition state must be then performed with singlet carrier and triplet oxygen.

The compounds consist of 72 and 74 atoms, respectively. This makes very difficult both to evaluate the vibration dependant thermochemical phenomena and to perform transition state search with eigenvector following method in reasonable time. Therefore, an additional computational study was performed in order to find a smaller group that could replace the triphenylphosphine group. This smaller group should approximate the electrostastical charge of the phosphorous atom. It is known that phenyl group exhibits a negative inductive effect. In spite of this fact, electrostatic charge in phosphor is negative as represented in Table 4.4. Some group candidates that might appropriately withdraw electrons are given in the continuation of the Table 4.4, where respective calculated charges are represented (Mulliken and natural charges can be considered as a further help in order to appropriately select the exchange group).

Interestingly, only trimethylphosphine and trifluoromethylamine groups come in question for the group replacement. For methyl groups, this is particularly surprising because of their positive inductive (+I) effect. Trifluoromethyl group, however, is expected to display (-I) effect. Less accurate calculation on AM1 and HF 3-21G(d) level also suggests to use P(CH$_3$)$_3$ and N(CF$_3$)$_3$ groups, but this additional approach was rejected because no further insights could be won from these calculations.

Now having the two groups chosen, we should first look at what is the group exchange effect on overall reaction enthalpy. The methyl group exchange results in -68.03 kJ/mol

---

8In advanced quantum chemistry programs, an option of charged ghost atoms can be applied instead of group exchange. However, this option is difficult to use properly.
Table 4.4: Different charge assignments on phosphorous atom in several groups assessed by Spartan’s B3LYP method, using 6-31g(d) basis set

<table>
<thead>
<tr>
<th>group</th>
<th>Mulliken</th>
<th>electrostatic</th>
<th>natural</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(Ph)₃</td>
<td>0.324</td>
<td>-0.547</td>
<td>0.903</td>
</tr>
<tr>
<td>PH₃</td>
<td>-0.092</td>
<td>-0.207</td>
<td>0.015</td>
</tr>
<tr>
<td>PCl₃</td>
<td>0.470</td>
<td>0.302</td>
<td>0.798</td>
</tr>
<tr>
<td>P(CN)₃</td>
<td>0.632</td>
<td>0.202</td>
<td>0.890</td>
</tr>
<tr>
<td>P(CF₃)₃</td>
<td>0.378</td>
<td>-0.152</td>
<td>0.651</td>
</tr>
<tr>
<td>P(CCF)₃</td>
<td>0.400</td>
<td>0.178</td>
<td>0.962</td>
</tr>
<tr>
<td>P(CCH)₃</td>
<td>0.378</td>
<td>0.080</td>
<td>0.961</td>
</tr>
<tr>
<td>P(CH₃)₃</td>
<td>0.404</td>
<td>-0.234</td>
<td>0.850</td>
</tr>
<tr>
<td>P(CF₂Cl)₃</td>
<td>0.441</td>
<td>-0.056</td>
<td>0.793</td>
</tr>
<tr>
<td>P(CCl₃)₃</td>
<td>0.676</td>
<td>-0.044</td>
<td>0.948</td>
</tr>
<tr>
<td>P(CH₂NO₂)₃</td>
<td>0.587</td>
<td>0.007</td>
<td>0.909</td>
</tr>
<tr>
<td>P(CCNO₂)₃</td>
<td>0.471</td>
<td>0.211</td>
<td>1.025</td>
</tr>
<tr>
<td>AsH₃</td>
<td>-0.151</td>
<td>-0.085</td>
<td>0.090</td>
</tr>
<tr>
<td>NH₃</td>
<td>-0.887</td>
<td>-1.011</td>
<td>-1.109</td>
</tr>
<tr>
<td>N(CH₃)₃</td>
<td>-0.351</td>
<td>-0.090</td>
<td>-0.494</td>
</tr>
<tr>
<td>N(CF₃)₃</td>
<td>-0.653</td>
<td>-0.350</td>
<td>-0.692</td>
</tr>
<tr>
<td>N(CCl₃)₃</td>
<td>-0.327</td>
<td>-0.074</td>
<td>0.544</td>
</tr>
</tbody>
</table>

(ECP) and -66.44 (DFT SCP) by BLYP method, both results being comparable to the energetics of original compound. In trifluoromethyl group exchange the reaction enthalpy is distorted down to -0.70kJ/mol, therefore these exchange are not to be considered any further.

The desired transition state search was thus performed on the compound with trimethyl-phosphine ligands. Unfortunately, TS could not be located. However, it seems that the reaction cannot be completed in a concerted manner but proceeds in at least two steps. From the evaluation of several TS optimisation trajectories, where different spin angular momenta were considered, I have found that oxygen does approach to the metal center with one of its electrons, very probably perpendicular to the CO-Cl ligands. This is shown in Fig. 4.12c. Later the constellation is rearranged to the „triangle-shaped” product (Fig.4.12c).

Parallel approach of oxygen is possible, but as an event also highly improbable. In the best case, the absolute magnitude of negative enthalpy of the reaction equals the positive activation energy.

Conclusion: The reaction of oxygen with Vasca compound is exothermic (-60 kJ/mol) and can be compared to oxygen reaction with Co-Salen. However, there exists a considerable reaction barrier of approximately 50 kJ/mol or more. The exact transition state could not be found. The group exchange method proved to be the reasonable approach for minimisation of computational time.

Finally, let me explain another principle of reducing the computational cost. I will use the
original Vasca compound for the demonstration purpose. The most interesting finding in this study comes from the vibrational analysis, which leads to the assessment of thermochemistry. Performing the calculation of vibrational spectrum is computationally much more expensive, especially when performed on the same (ab-initio or DFT) computational level, than the calculation of subsequent electronic energy approaching equilibrium structure (assuming reasonable initial guess) and actually, only this is acceptable approach according to several textbooks. We shall look now at the entropy at 298.15 K and 1 bar for the adduct only. The „correct” values, as they are seen in the Table 4.5, have been calculated on the same level of theory as the geometry optimisation was performed and the shortcut method was conducted by Spartan on PM3 level as a single point frequency calculation on established geometries. Whereas the shortcut method could be completed within an hour, all other tasks lasted for more than 3 days on the single processor. The same is also valid for corrections to the enthalpy and corrections to the Gibbs free enthalpy, since these values depend on molecular mass (translational contribution), geometry (rotational contribution), forces between atoms (vibrational contribution) and on pressure and temperature.
Table 4.5: Correct assessment of entropy values compared to the value obtained by the shortcut method

<table>
<thead>
<tr>
<th>software</th>
<th>entropy [J/mol K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMol3 (DFT)</td>
<td>1039.3</td>
</tr>
<tr>
<td>Gaussian (DFT)</td>
<td>1151.4</td>
</tr>
<tr>
<td>Turbomole (DFT)</td>
<td>1124.4</td>
</tr>
<tr>
<td>shortcut (Spartan, PM3)</td>
<td>1033.0</td>
</tr>
</tbody>
</table>

Usage of this shortcut causes the flood of imaginary frequencies in the output of the cheap methods, which are all neglected in thermal corrections. Whereas the absence of negative normal modes confirms that one has obtained an energy minimum on potential energy surface, this shortcut can not be used for such confirmation. Nevertheless, it enables quick assessment of further data like $c_p$.

We will focus thermochemistry again later on another, more suitable compound in this chapter in more depth.

For more information on activated oxygen by compounds forming $\eta^2$-oxygen constellation, it should be referred to a theoretical review [193] and to a compilation of related catalysts [194].

### 4.2.2 Carriers for Olefins

In principle, two groups of carriers for olefins can be distinguished. The first group consists of inorganic and organic copper and silver salts, in the second group one finds sulfur complexes with different transition metals. My aim is to take a closer look on the mechanisms of interaction between known carriers and olefins, mainly because of its importance for general understanding and also for mathematical modelling of carrier membrane processes.

#### Common features of copper and silver salts

The simplest system to begin with is the lowest olefin, ethylene, adsorbing on the hypothetical gas phase ions $Ag^+$ and $Cu^+$. In Fig. 4.13a, sorption path energetics calculated by DTF method with B3LYP functional and 6-31G*/LANL2DZ basis set is shown. When the pseudopotential (ECP, LANL2DZ) for copper is not used, unrealistically high reaction enthalpy is obtained. For the mechanism, since no transition state can be located, this implies physical sorption rather than a chemical reaction. The magnitude of the enthalpy, however, suggests chemical adsorption. During adsorption, the length of the double bond increases but will not be broken. Therefore, the formal definition of the actual physical interaction remains the subject of controversy. For the interaction of double bond with salts of transition metals Pd, Pt, Hg, Cu and Ag, one observes the straightforward conservation of orbital symmetry, a clue for a favoured reaction [195]. Whereas in Zeise's salt ($KPtCl_3$),
PtCl$_3^-$ coordinates ethylene via quasi sigma bond (-142,55 kJ/mol) (Fig. 4.13b, in Ag$^+$ and Cu$^+$ (Fig. 4.13c) the reversible bonding occurs via coordinative $\pi$-backdonation, cf. [196, 197, 198]. This can be seen as the confirmation for adsorption mechanism.

Figure 4.13: Ethylene adsorption on gas phase Ag and Cu cations: a) sorption path energetics; b) HOMO orbitals in PtCl$_3^-\text{Et}$ anion; c) HOMO orbitals before and after the postulated transition state in Cu$^+$-Et cation

Independently of the formal definition assignment, evaluation of reaction paths without transition state is only possible by the means of constrains imposed to the molecular system. Without the usage of distance/bond, ligand or angle constraints (bc, lc, ac) or partial freezing of atom positions (f) (Fig. 4.14a) energy minimisation calculation would always yield only the global minimum.

Figure 4.14: Calculation of ethylene adsorption to the chosen gas phase Ag(I) and Cu(I) salts: a) usage of constrained optimisation technique; b) sorption path energetics

For illustration, in Fig. 4.14b two more examples about adsorption path energetics are given. Here, also no transition state was found. In case of AgBF$_4$, ligand distance from metal center being between 3,8 and 4,8 Å, so called wavefunction oscillation can be observed. In this region, the calculation does not readily converge. The cause for what
is believed to be the loose transition state in this constellation may be the difficulty of electrons to occupy orbitals according to the aufbau principle. Since both reactants are singlets, the transition state is also singlet. However, restricted singlet calculation was performed on this system. The oscillation could be overcome by performing computationally more expensive unrestricted singlet calculation, but without additional gain of information.

Copper salts

It is today well known that ethylene is an important plant hormone taking part in growth, germination and fruit ripening [199]. The exact site of ethylene action has not been found yet. However, the ethylene-binding domain in the respective proteins (e.g. ETR1) is unambiguously associated with the presence of copper(I) ions [200], although several experts claim that such membrane bound interactions are purely physical effects [201]. Since there is no experimental data on molecular environment of copper in such proteins, biomimetics as in case of oxygen is not feasible either experimentally nor theoretically. Since copper(I) in aqueous solutions is prone to disproportionate to elemental copper and copper(II) [202], an effective redox mechanism in-vivo must therefore exist in order to keep the site active.

Many experimental attempts were undertaken in order to synthesise chelate copper compounds instead of simple copper (I) salts that form complexes with olefins (cf. [203]). The syntheses were all, without exception, conducted in dry nitrogen using the standard Schlenk or vacuum line technique for prevention of the undesired disproportionation reaction. For industrial applications of olefin removal or separation, the successful usage of absolutely water free non-aqueous chemical solvents was reported, where copper(I) salts do not disproportionate. Several copper carriers were already thoroughly investigated [71] in this context, but were not primarily intended to be used with membranes. Some attempts using nanofiltration membranes modified by CuCl were reported [204], unfortunately with very low selectivities.

Another work-around method, where disproportionation reaction of copper (I) cation in aqueous environment can be controlled, is electrochemical modulation [205]. However, this approach cannot easily be used in facilitated transport membranes.

Apart from the deactivation reaction by disproportionation, the most important feature seems to be sufficiently high solubility of copper(I) complexes in appropriate solvents. Therefore, in addition to the ligand and anion choice, chemical environment plays an important role. In quantum chemistry, e.g. PCM is used for treatment of solvation effects. Table 4.6 shows the reaction enthalpies ($\varepsilon_0 + \varepsilon_{ZPVE}$) without finite temperature thermal corrections for a variety of anions in the ideal gas phase and in an exemplary solvent (propanenitrile, permittivity constant $\varepsilon_r = 29.7$ [92]). One can see that adsorption enthalpy for this reaction does not significantly depend on the polarity of the surrounding medium. This might be due to the insensitivity of the computational method.

Experimentally determined reaction enthalpy values for these reactions, however, lie around -34 kJ/mol.
Table 4.6: The influence of the anion choice on ethylene-copper(I) complexation reaction enthalpies in vacuum (v) and in propanenitrile (pn) (BP, def-TZVP; COSMO-PCM)

<table>
<thead>
<tr>
<th>anion</th>
<th>$\Delta H$ (v) [kJ/mol]</th>
<th>$\Delta H$ (pn) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>-166.3</td>
<td>-175.7</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>-198.3</td>
<td>-197.4</td>
</tr>
<tr>
<td>SO$_4^-$</td>
<td>-194.1</td>
<td>-185.3</td>
</tr>
<tr>
<td>BF$_4^-$</td>
<td>-204.0</td>
<td>-212.3</td>
</tr>
<tr>
<td>AlCl$_4^-$</td>
<td>-145.8</td>
<td>-170.5</td>
</tr>
<tr>
<td>PF$_6^-$</td>
<td>-193.4</td>
<td>-218.2</td>
</tr>
<tr>
<td>SbF$_6$</td>
<td>-191.3</td>
<td>-220.2</td>
</tr>
<tr>
<td>PO$_2$F$_2$</td>
<td>-195.9</td>
<td>-181.3</td>
</tr>
<tr>
<td>FSO$_3^-$</td>
<td>-193.3</td>
<td>-198.8</td>
</tr>
<tr>
<td>CH$_3$SO$_3^-$</td>
<td>-190.3</td>
<td>-185.6</td>
</tr>
<tr>
<td>CF$_3$SO$_3^-$</td>
<td>-190.1</td>
<td>-192.4</td>
</tr>
<tr>
<td>PhSO$_3^-$</td>
<td>-190.5</td>
<td>-177.4</td>
</tr>
<tr>
<td>MePhSO$_3^-$</td>
<td>-189.8</td>
<td>-186.1</td>
</tr>
<tr>
<td>CH$_3$CH$_2$SO$_3^-$</td>
<td>-190.1</td>
<td>-185.7</td>
</tr>
<tr>
<td>CH$_3$CO$_2$</td>
<td>-186.4</td>
<td>-181.3</td>
</tr>
<tr>
<td>CF$_3$CO$_2$</td>
<td>-184.8</td>
<td>-173.2</td>
</tr>
<tr>
<td>CF$_3$CF$_2$CO$_2$</td>
<td>-184.4</td>
<td>-183.7</td>
</tr>
<tr>
<td>Salicylate</td>
<td>-185.8</td>
<td>-184.6</td>
</tr>
<tr>
<td>Di(t-butyl)salicylate</td>
<td>-187.7</td>
<td>-188.4</td>
</tr>
</tbody>
</table>

Ionic liquids as non-aqueous solvents with quite variable dielectric properties might also be appropriate environment, where copper(I) salts could remain active and would not disproportionate. The main drawback of this consideration is to find good soluble copper(I)-based compounds with reasonable molecular mass. Solubilities must still be determined experimentally.

*Copper(I)tetrachloroaluminate* Above, I have treated copper(I)-ethylene complexes in their usual stoichiometry ratio 1:1. Interestingly, the existence of di-olefine complexes was claimed for comparable silver compounds (e.g., Ag(C$_2$H$_4$)+) [206], but these were never observed in more than analytical quantities. Recently, it was shown experimentally that solid CuAlCl$_4$ is able to reversibly bind two equivalents of ethylene in a consecutive reaction [207] at technically relevant temperatures. Of particular importance is the melting point of the compound (42°C) and the observed reversibility of the reaction at 65°C accompanied by noticeable effervescence. At these temperatures, having a melt, we would have an ionic liquid with low vapor pressure. Some structural crystal data is available for cuprous di-ethylene complexes. I have used this information for calculations in the

---

9In order to check the reliability of a certain computational method, the first step is often to look up experimentally determined structural data and compare them to results from test calculations. For instance, data from X-ray diffraction experiments correspond to computed electron density around heavy atoms, which is usually represented as contour plot.
4.2. KNOWN CARRIERS

gas phase looking both at geometry and at the reaction energetics. The geometries of the respective products are shown in Fig. 4.15. Note the difference between the „cis”, the „trans” and the symmetric „sym” product.

Figure 4.15: Ethylene addition to CuAlCl$_4$: gas phase structures of adduct with a) one olefin as well as with b), c) and d) two olefin molecules

The complete results of the conducted calculations are given in Tab. 4.7. Interestingly, both DFT methods give „cis” and „trans” products. HF calculation results in fully symmetrical product. In MP2 method, only „trans” form could be brought to convergence.

Table 4.7: Reaction energies $\Delta H$ calculated by different methods implemented in Spartan (6-31+G(d)) and DMol$^3$ (AER, DNP)

<table>
<thead>
<tr>
<th>method</th>
<th>mono [kJ/mol]</th>
<th>di „sym” [kJ/mol]</th>
<th>di „cis” [kJ/mol]</th>
<th>di „trans” (pn) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>-117,7</td>
<td>-</td>
<td>-29,88</td>
<td>-28,74</td>
</tr>
<tr>
<td>HF</td>
<td>-66,15</td>
<td>-26,52</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MP2</td>
<td>-153,5</td>
<td>-</td>
<td>-</td>
<td>-8,45</td>
</tr>
<tr>
<td>BLYP (DMol$^3$)</td>
<td>-183,1</td>
<td>-</td>
<td>-59,45</td>
<td>-57,46</td>
</tr>
</tbody>
</table>

I also attempted to locate transition states with DMol$^3$ by applying its LST/QST method. Indeed, a transition state with appropriate normal mode vibration (-1,11 cm$^{-1}$!) for the first reaction step (mono) could be located, but at (unreasonable) ethylene distance from copper atom of 12,36 Å and negative activation energy of -21 kJ/mol. This result would suggest that the transition state is more stable than the reactants and less stable than the product, what may be - again - put in accordance with the theory of loose transition state.

The transition state for the „cis” product could also be found with the normal mode of -61,43 cm$^{-1}$ and activation energy of 5,23 kJ/mol, whereas for the „trans” products all attempts failed. The reverse reaction from the „cis” product back to mono has an activation energy of 64,77 kJ/mol.
Conclusion: According to these calculations it is surprising that di-olefin complexes of related compounds were not found experimentally more often. The energetics for this reaction is favourable both in respect to the enthalpy and the activation energy - even for the second step.

Ligand-based copper carrier salt The perchlorate of Cu(I)(3,4,7,8-tetramethyl-1,10-phenanthroline) \( [203] \) is, in contrast to propanenitrile solvated copper cation, an example of internally stabilised core metal. The bidentate ligand provides more defined and more stable chemical environment for the metal as molecules of propanenitrile, whose residence time for the coordination is the subject of fluctuations in overall operating conditions. The calculation with BP (GGA) functional using def-TZVP basis set yielded reaction enthalpy of \(-174.2\) kJ/mol. Although the reaction itself does not show any particular behavior, this kind of compounds are electronically soft. Considering the Pearson's concept of soft acid and basis, this concept might be equally applied to approach qualitative behaviour of solubilities\(^10\). Therefore, such electron rich compounds with may be therefore ideally suited for applications with ionic liquids as solvents in order to obtain sufficient compound solubilities, which are often not given for hard salts (e.g. CuCl). For detailed treatment, please refer to the section 4.3.7.

Silver salts

Paraphrasing \([208]\), the subject of this section could also be called „membrane separations of olefins from paraffins based on silver salts - 40 years looking back in anger”. Many attempts were undertaken in manufacturing of membranes using silver salts filled in different materials. So far, no commercial products could be scored. There are two problems with silver: the first is its deactivation and the second is the required aqueous environment for the reaction to take place, i.e. feed mixture must be humidified. In paraffin/olefin separation, humidification of the feed hydrocarbons does not seem reasonable, since the removal of traces of water from the permeate would cause additional problems and costs.

The scope of investigated silver anions is not as high as in case of copper. However, silver chemistry in general seems to be more transparent \([209]\)\(^11\) and furthermore, several attempts in the development of silver based industrial separation for olefins are known \([211]\). As already said: whereas copper requires water free environment, silver salts can and even must be used in the presence of water. The main drawback of silver salts is their strong reducing capacity, which is induced through the daylight.

In Table 4.8, results for the reaction enthalpy obtained by BP functional of different silver salts with ethylene are shown. Obviously, the species become more reactive in aqueous environment by up to \(40\) kJ/mol. Furthermore, for the purpose of comparison, more realistic reaction enthalpies for selected salts were calculated with B3LYP functional, approaching experimentally obtained values (around \(-28\) kJ/mol) \([212, 171, 213]\). These

\(^{10}\)In case this approach fails, one can use the „nasty” chemistry from the beginning of 20\(^{th}\) century and sulfonate the heterocycle, since it is known that sulfonated compounds are likely to be dissolved in ionic liquids.

\(^{11}\)A more general treatment of reactions where different reactants are added to the bicyclic olefins can be found in \([210]\).
values and those obtained by BLYP functional using numerical basis set are also corrected for finite temperatures, here 298.15 K.

Table 4.8: The influence of the anion choice on ethylene-silver(I) complexation reaction enthalpies in vacuum (v) and in water (w) (BP def-TZVP Turbomole (T); B3LYP 6-31G*/LANL2DZ Spartan (S); B3LYP 6-31G*/LANL2DZ Gaussian (G); BLYP DND/all electron DMol\(^3\) (D))

<table>
<thead>
<tr>
<th>anion</th>
<th>(\Delta H_0) (v,T) [kJ/mol]</th>
<th>(\Delta H_0) (w,T) [kJ/mol]</th>
<th>(\Delta H) (v,S) [kJ/mol]</th>
<th>(\Delta H) (v,G) [kJ/mol]</th>
<th>(\Delta H) (v,D) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbF(_6^–)</td>
<td>-120,7</td>
<td>-176,5</td>
<td>-100,4</td>
<td>-98,9</td>
<td>-70,5</td>
</tr>
<tr>
<td>PF(_6^–)</td>
<td>-122,1</td>
<td>-164,4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BF(_4^–)</td>
<td>-128,7</td>
<td>-172,6</td>
<td>-103,7</td>
<td>-90,7</td>
<td>-73,5</td>
</tr>
<tr>
<td>SiF(_6^–)</td>
<td>-125,4</td>
<td>-135,4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ClO(_4^–)</td>
<td>-128,3</td>
<td>-111,4</td>
<td>-104,8</td>
<td>-92,5</td>
<td>-118,1</td>
</tr>
<tr>
<td>CF(_3)CO(_2^–)</td>
<td>-117,3</td>
<td>-143,8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO(_3^–)</td>
<td>-130,8</td>
<td>-151,7</td>
<td>-104,8</td>
<td>-92,5</td>
<td>-118,1</td>
</tr>
<tr>
<td>BrO(_3^–)</td>
<td>-114,2</td>
<td>-131,8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl(^–)</td>
<td>-110,3</td>
<td>-134,9</td>
<td>-90,6</td>
<td>-81,1</td>
<td>-90,8</td>
</tr>
</tbody>
</table>

The newest concepts with tailored, i.e. task specific ionic liquids, (zwitterionic silver complex in form of imidazolium salt [214]) might represent the new opportunity for the breakthrough, but must prove themselves stable.

**Transition metal carriers with sulphur ligands**

Two already known carriers, which can nevertheless be considered to be alternatives to the silver and cooper salts, are discussed in this section. These carriers were never used in membrane applications.

*Nickel dithiolene compound:* This transition metal complex that was firstly discovered in 1963 [215] is able to reversibly bind strained olefines [216] and conjugated dienes [217]. In contrast to the carriers treated so far, the olefine double bond does not coordinate the central metal but instead rather reacts with two of the four sulfur ligands in a cycloaddition [2+3] reaction. In principle, several bonding patterns are possible. Double bond can bind either to the atoms 1 and 2 or to the atoms 1 and 4 (Fig. 4.16a), whereas the distance between the atoms 2 and 4 seems to be prohibitive for the bond formation (please, mind the molecule’s symmetry). In case of propylene, four, and in case of norbornadiene eight attachment possibilities to these sulfur atoms exist, considering all exo, endo, cis and trans arrangements. Attachment to the atoms 1 and 4 is energetically highly disadvantageous, since the otherwise planar carrier complex is forced to bend according to sp\(^2\)-sp\(^3\) hybridisation change on the respective sulfur atoms. Computationally estimated energy penalty for that kind of bending lies between 40 to 60 kJ/mol, depending on the bulkiness of the olefine. Interestingly, the experimentally observed norbornadiene adduct which will be considered here is not computationally the most stable one. However, difference to the lower lying analogues is with only 4 kJ/mol rather small. Butadiene must be in its
thermodynamically less stable cis form in order for the cycloaddition reaction [3+4] to take place. Here, among many attachment modes, only those two to atoms 1 and 2 are considered.

![Figure 4.16: Nickel dithiolene compound a) basic structure b) frontier orbitals for the carrier (LUMO), the alkene (HOMO) and the diene (HOMO) (the phases of wavefunction are denoted by + and -) (Image)](image)

Calculated frontier orbitals that determine reaction behaviour are shown in Fig. 4.16b. Predicting behaviour from Woodward-Hofmann rules, it can be stated that the addition is only thermally allowed when the two approaching molecules can interact with their wavefunction phases being of the same sign (this explanation is a bit of an oversimplification, just to make the rules understandable). Therefore, the reaction is forbidden for the addition of the monooolefine to the atoms 1 and 2 but allowed for its addition to the atoms 1 and 4. Conjugated dienes can attach to the atoms 1 and 2, in principle also to 1 and 3 but not to 1 and 4.

Computational study covering the species’ stability and the most of the thermodynamics was performed with B3LYP functional and 6-31G(d) basis set with Gaussian software. Gas phase calculations were performed and Onsager solvation model was applied. Recommended solute volume was taken from gas phase calculations and cyclohexane was chosen as solvent. The forbidden reaction to norbornadiene adduct is only possible due to the internal ring tension (reaction enthalpy is ca. -77 kJ/mol). The addition of monooolefine can not be observed at ambient conditions due to the unfavourable reaction enthalpy being ca. -24 kJ/mol for propylene and ca. -45 kJ/mol for norbornadiene. All enthalpy values are not corrected for the thermal effects. Full evaluation, however, where explicit thermodynamic values are taken into account, is shown in Fig. 4.17a. Explicit thermodynamic values means applying of non-approximated reaction enthalpies at the temperature in question, which do change with temperature and are not approximated by van’t Hoff equation. The values for free Gibbs enthalpy that increase with increasing temperature are then taken to calculate equilibrium constant according to:

\[ K_a = e^{-\frac{\Delta G^o}{RT}} \]
4.2. KNOWN CARRIERS

One can clearly see that, assuming the correctness of the acquired data, the reaction with norbornadiene can take place spontaneously at temperatures below 350°C and that the other two reactions can not take place at all. On the other hand, equilibrium constant increases with decreasing temperature. The presence of solvent increases the reaction enthalpy and therefore also the reaction free Gibbs enthalpy.

![Graph showing thermodynamic quantities](image)

Figure 4.17: Addition of propylene, butadiene and norbornadiene to nickel dithiolene compound a) in terms of energetics (here exemplary for liquid phase) and b) in terms of ideal equilibrium constant in gas and liquid phase

But can the data really be brought in line with experimental findings? Structure cross cheque is shown in Fig. 4.18 by comparison of ab-initio, DFT and hard data from x-ray spectroscopy [218]. The smallest error in the calculated distances and angles is achieved at the DFT level with the smallest basis set, but all the calculations reproduce the geometry surprisingly well. Furthermore, the comparison of energetics was performed with different software and at different levels of theory. The larger the basis set used, the more accurate seems to be the calculation (note the similar trends between B3LYP 6-311++G(2d,2p), BP def-TZVP and BP DNP). However, it is again not possible to decide, which method to take for exact evaluation of thermochemistry.

Finally, I would like to discuss the search for a transition state. Density functional studies with BLYP functional in DMol³ software show concerted reaction path, where the addition reaction display a mirror symmetry. A single imaginary frequency of -331,57 cm⁻¹ (BLYP) emerged from vibrational analysis, activation energy being 81 kJ/mol.

The indication that the found transition state corresponding to the concerted reaction is not the true transition state, can be shown by applying (more conservative) HF or (hybrid) B3LYP calculation to the hypothetical transition state. In Gaussian calculation, providing the final TS structure from DMol³, HF transition state optimisation was performed and was not brought to convergence within 62 cycles. The structure gained is not symmetric leading to the conclusion that the reaction must be accomplished within at least two distinguished steps! This was also confirmed by Turbomole BP SV(P) calculation, where the apparent TS was found (- 504,6 cm⁻¹; $E_A= 96,9$ kJ/mol), but it was not symmetric and furthermore norbornadiene seemed suspiciously relaxed. What to do now with this discrepancy? In closely related test calculations, i.e. on [2+2] cycloaddition reactions,
similar behavior was also found. It could be impressively shown that e.g. the ethylene dimerisation reaction to cyclobutane and its reverse reaction within HF theory is indeed of rotatoric nature, whereas DFT calculation with BP functional and numerical basis set „allows” theoretically forbidden smooth reaction [219, 220]. From this findings I can draw the conclusion that the non-hybrid DFT calculations often violate the orbital symmetry and give non-existent transition states.

Recently [221], a new, electrochemical way that provides on/off switch for binding of ligands, in particular of monoolefines, was reported for the above nickel dithiolene complex. By adding or removing electrons from the complex in an electrochemical process reminding cyclovoltametry, it can selectively bind the olefines in oxidised and release them in reduced state, all reactions now being allowed - as they would be in the photochemical reaction with neutral molecule. At the same time, poisoning with H₂S, H₂O or CO is reported not to take place.

Although the discovery of electrochemical switch is without doubt very interesting and might have a great impact on research of similar behavior in other compounds [222], this does not solve the realisation problem for the technical equipment. Electrochemical switch is not easily feasible" in supported liquid membrane arrangement [226].

---

12A suggestion can be made here that silicone rubber filled with graphite might provide a solution to this problem, where it can act both as a non-selective permeable membrane and an electrical contact.
An interesting combination might be the ionic liquids and the electrochemical switch in the arrangement of membrane contactor. It must be noted, however, that the compound is not easily synthesised C.3 and is, apart from „nasty synthetic chemistry”, comparably expensive.

*Molybdenum sulfur bridged compounds:* Firstly being brought in connection with hydrosulfurisation reactions as catalysts, stable hydrogenated forms from this highly interesting compound family showed substitution reaction when combined with unsaturated molecules (ethylene and acetylene) [227]. From this point on, further studies were performed that revealed that the addition of double bond does not necessarily need to be a (technically useless) exchange reaction [228]13. Experimentally, quite high equilibrium constants were found for the reversible addition of ethylene at room temperature and ambient pressure, making these compounds attractive as potential carriers for membrane separations. Later on, kinetic - but not thermodynamic - studies of reversible olefin binding to the sulfido sites were reported [229]. The compound of interest together with molecular orbitals is shown in Fig. 4.19. In contrast to the previously treated compound this reaction is allowed and concerted.

Figure 4.19: Molybdenum compound: a) and b) two views on reactant’s structure with its LUMO molecular orbitals and c) transition state with ethylene

The reaction enthalpy with ethylene based on electronic energy only yielded -100,37 kJ/mol with Gaussian and -103,22 kJ/mol with Spartan, both calculations being performed with B3LYP/6-31G(d). Thermal corrections for 1 bar and 298,15 K gives final reaction enthalpy of -91,12 kJ/mol and Gibbs free enthalpy -of 35,54 kJ/mol. Exact transition state with imaginary frequency of -181,9 cm\(^{-1}\) leads to the activation energy of 15,15 kJ/mol and 20,5 kJ/mol for corrected value, respectively. Note that the ethylene forms dihedral angle (1-2-3-4) of 180° with the sulfur atoms. Another imaginary frequency -10,9 cm\(^{-1}\) arises form the relative motion of two cyclopentadienyl ligands to each other. This mode can be, also due to its low intensity, neglected.

---

13Under such an exchange reaction one understands the exchange of one olefin that is already bound to the complex with another one, which shows higher equilibrium constant than the former one.
The substitution of one hydrogen one each cyclopentadienyl ligand with methyl group causes slight deactivation (-98.49 kJ/mol), the same substitution with nitro group causes strong activation (-161.69 kJ/mol) of the compound. Here, the feasibility of the syntheses with nitro-substituted cyclopentadienyls were not considered. The advantage of these compounds might be their stability, the main disadvantage is multistage synthesis and expensive reactants.

The reaction of ethylene with this compound is a very good example for letting me introduce the complete temperature dependant evaluation of thermodynamics and kinetics according to the established theories. Some experimental data is also available, therefore we might loosely compare those results with computational ones where applicable. For ethylene, equilibrium constant $K_c(\text{!})$ of $> 3 \cdot 10^4$ dm$^3$/mol and $k_{\text{add}}$ of 19 dm$^3$/mol s at ambient conditions, but in different solvents was reported. For propylene, activation enthalpy $\Delta H^\ddagger$ is 89 kJ/mol and activation entropy $\Delta S^\ddagger$ -24 J/(mol K), respectively. That value will be applied for ethylene as well since we have no better choice. My calculations apply to gas phase.

Again, it proved that DFT calculations with different software yield different results. In addition to Gaussian calculation above, Turbomole was used on BP level with SV(P) basis set. Hereby, the reaction enthalpy with ethylene based on electronic energy yielded only -68.9 kJ/mol. Correction for zero point gave -57.7 kJ/mol. Thermal corrections for 1 bar and 298,15 K results in the final reaction enthalpy of -50.5 kJ/mol and free Gibbs enthalpy of +6.9 kJ/mol. Exact transition state with imaginary frequency of -138.6 cm$^{-1}$ leads to the activation energy of 3.2 kJ/mol and 7.5 kJ/mol for the corrected value. As above, imaginary frequency at -9.5 cm$^{-1}$ is also present. Thus, we cannot assume that the values for the electronic energies are correct. In Fig. 4.20, full temperature dependance of thermodynamic quantities and kinetics is presented as obtained with Turbomole. One can notice that reaction enthalpy changes little with temperature and that the often applied van’t Hoff approximation

$$\frac{\partial \ln K_a}{\partial T} = \frac{\Delta H_r}{RT^2}$$

is indeed a good one. The results by applying this approximation with implemented equation

$$K_a(T_2) = e^{\ln K_a(T_1)} + \frac{\Delta H_r}{R} \cdot \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

are denoted in Fig. 4.20a with crosses. According to both these calculations, the reaction will take place spontaneously only below 275 K.

For kinetics, the activation energy $E_a$ is typically taken to be independent of temperature and equals the difference of molecular zero point energies ($\varepsilon_0 + \varepsilon_{\text{ZPVE}}$) [231]. This consideration is reasonable because the Boltzmann occupation of higher discrete energy levels due to the temperature does not play an important role. Sometimes, when no other data

$^{14}$It should be noted that further „carriers” were proposed by the same group working on molybdenum compounds [229], which show comparable properties. For five-coordinated Pt(II)(C$_2$H$_4$)Cl$_2$(bipy) and CpReO(diolate), see also [230]. The later compound adds ethylene only at very low temperatures.
4.2. KNOWN CARRIERS

Figure 4.20: Ethylene addition to molybdenum compound: a) „true” thermodynamics and b) kinetics based on Turbomole calculation c) van’t Hoff approximation used for $K_a$ from Gaussian calculation based on results at 1 bar and 298.15 K and calculation of very distorted $\Delta G_r$ from this data

is available, activation energy is approximated with temperature dependent enthalpy of activation, too. Completely unreasonable results are, however, obtained by classical thermodynamic reasoning, where temperature dependant free Gibbs enthalpy of activation is considered (partition functions are taken into account twice in this case, which is not allowed!). In my Turbomole calculation, the reaction rate of 767.5 dm$^3$/(mol s) at 300 K is obtained. Gaussian pendant calculation gives 4.95 dm$^3$/(mol s), which is much closer to the experimental value. In contrast to the calculation of $K_a$, exact application of the transition state theory gives directly the correct units for reaction rate of bimolecular reaction. The application of transition state theory for the kinetics calculation of the reverse reaction is not possible, since we have here a molecular decay, which is a monomolecular reaction.

The results of conversion of the quantum mechanically calculated thermodynamic equilibrium constant $K_a$ to $K_p$ for the molybdenum compound reaction with ethylene - formally calculated for the ideal gas phase - are shown in Table 4.9. For the procedure of how the conversion is performed in practical engineering work, one should refer to the theory ([232], Chapter 8). Apart from being not able to define an appropriate standard states in
terms of pressure and concentration, we also operate in a liquid phase: a further conversion of experimental $K_p$ to $K_c$ requires the exact knowledge of (concentration dependent) density or partial molar volumes of the system’s components (for conversion of concentrations $c_i$ to mol fractions $x_i$) and, if the system is additionally treated as non-ideal mixture, of activity coefficients $\gamma_i$ [142]. The later can be approximately obtained from COSMOtherm calculation, but since we do not know the real value of $\Delta_nG$, all the efforts for obtaining reliable information, which could be brought in line with experimental results, as in case of oxygen-carrier, are in vain. Published $K_c$ values, which have been determined experimentally, therefore can not be correlated to $K_a$ without knowing the exact experimental conditions.

Table 4.9: Temperature dependence of equilibrium constants expressed as $K_p$ and $K_a$ (Turbomole calculation)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-49,117</td>
<td>-30,946</td>
<td>9,393·10^{-6}</td>
<td>9,393·10^{-1}</td>
<td>1,459·10^{16}</td>
</tr>
<tr>
<td>125</td>
<td>-49,525</td>
<td>-26,356</td>
<td>4,593·10^{-10}</td>
<td>4,593·10^{-15}</td>
<td>1,031·10^{11}</td>
</tr>
<tr>
<td>150</td>
<td>-49,863</td>
<td>-21,686</td>
<td>2,614·10^{-6}</td>
<td>2,614·10^{-11}</td>
<td>3,561·10^{7}</td>
</tr>
<tr>
<td>175</td>
<td>-50,141</td>
<td>-16,966</td>
<td>2,432·10^{-3}</td>
<td>2,432·10^{-8}</td>
<td>1,158·10^{5}</td>
</tr>
<tr>
<td>200</td>
<td>-50,339</td>
<td>-12,216</td>
<td>1,229·10^{-1}</td>
<td>1,229·10^{-6}</td>
<td>1,550·10^{3}</td>
</tr>
<tr>
<td>225</td>
<td>-50,467</td>
<td>-7,436</td>
<td>2,046·10^{-1}</td>
<td>2,046·10^{-4}</td>
<td>5,324·10^{3}</td>
</tr>
<tr>
<td>250</td>
<td>-50,555</td>
<td>-2,646</td>
<td>7,664·10^{-3}</td>
<td>7,664·10^{-2}</td>
<td>3,571</td>
</tr>
<tr>
<td>275</td>
<td>-50,572</td>
<td>2,144</td>
<td>5,029·10^{-4}</td>
<td>5,029·10^{-5}</td>
<td>3,915·10^{-1}</td>
</tr>
<tr>
<td>300</td>
<td>-50,540</td>
<td>6,924</td>
<td>5,391·10^{-5}</td>
<td>5,391</td>
<td>6,229·10^{-2}</td>
</tr>
<tr>
<td>325</td>
<td>-50,478</td>
<td>11,724</td>
<td>7,986·10^{-6}</td>
<td>7,986·10^{-1}</td>
<td>1,305·10^{-2}</td>
</tr>
<tr>
<td>350</td>
<td>-50,386</td>
<td>16,504</td>
<td>1,540·10^{-6}</td>
<td>1,540·10^{-1}</td>
<td>3,443·10^{-3}</td>
</tr>
<tr>
<td>375</td>
<td>-50,234</td>
<td>21,264</td>
<td>3,868·10^{-7}</td>
<td>3,868·10^{-2}</td>
<td>1,092·10^{-3}</td>
</tr>
<tr>
<td>400</td>
<td>-50,072</td>
<td>26,024</td>
<td>1,134·10^{-7}</td>
<td>1,134·10^{-2}</td>
<td>3,996·10^{-4}</td>
</tr>
<tr>
<td>425</td>
<td>-49,870</td>
<td>30,784</td>
<td>3,850·10^{-8}</td>
<td>3,850·10^{-3}</td>
<td>1,646·10^{-4}</td>
</tr>
<tr>
<td>450</td>
<td>-49,647</td>
<td>35,524</td>
<td>1,493·10^{-8}</td>
<td>1,493·10^{-3}</td>
<td>7,526·10^{-5}</td>
</tr>
<tr>
<td>475</td>
<td>-49,425</td>
<td>40,244</td>
<td>6,244·10^{-9}</td>
<td>6,244·10^{-4}</td>
<td>3,754·10^{-5}</td>
</tr>
<tr>
<td>500</td>
<td>-49,173</td>
<td>44,954</td>
<td>2,889·10^{-9}</td>
<td>2,889·10^{-4}</td>
<td>2,012·10^{-5}</td>
</tr>
<tr>
<td>525</td>
<td>-48,891</td>
<td>49,664</td>
<td>1,462·10^{-9}</td>
<td>1,462·10^{-4}</td>
<td>1,140·10^{-5}</td>
</tr>
<tr>
<td>550</td>
<td>-48,599</td>
<td>54,344</td>
<td>7,782·10^{-10}</td>
<td>7,782·10^{-5}</td>
<td>6,901·10^{-6}</td>
</tr>
<tr>
<td>575</td>
<td>-48,307</td>
<td>59,014</td>
<td>4,363·10^{-10}</td>
<td>4,363·10^{-5}</td>
<td>4,356·10^{-6}</td>
</tr>
<tr>
<td>600</td>
<td>-47,995</td>
<td>63,684</td>
<td>2,665·10^{-10}</td>
<td>2,665·10^{-5}</td>
<td>2,857·10^{-6}</td>
</tr>
<tr>
<td>625</td>
<td>-47,683</td>
<td>68,324</td>
<td>1,661·10^{-10}</td>
<td>1,661·10^{-5}</td>
<td>1,949·10^{-6}</td>
</tr>
<tr>
<td>650</td>
<td>-47,340</td>
<td>72,954</td>
<td>1,073·10^{-10}</td>
<td>1,073·10^{-5}</td>
<td>1,372·10^{-6}</td>
</tr>
<tr>
<td>675</td>
<td>-46,998</td>
<td>77,584</td>
<td>7,153·10^{-11}</td>
<td>7,153·10^{-6}</td>
<td>9,915·10^{-7}</td>
</tr>
<tr>
<td>700</td>
<td>-46,656</td>
<td>82,184</td>
<td>4,955·10^{-11}</td>
<td>4,955·10^{-6}</td>
<td>7,370·10^{-7}</td>
</tr>
</tbody>
</table>

Conclusion: Although the molybdenum compound displays a distinctive transition state, it is one of the best candidates to be tried as a carrier in liquid or solid matrix membrane. From the calculations it is clear, however, that a further activation is desirable. It was
shown that such an activation can be achieved by application of nitro or other groups with negative inductive effect. In contrast to the nickel compound above, one has here more flexibility in doing such an activation, since trifluoromethyl groups can hardly be exchanged for any better group. With this final suggestion we are turning to computational design of carriers, which is treated in the next section.

4.3 Computationally Designed Carriers

The search for new compounds that act as carriers was recently claimed to be necessary [233] in order to push the limits of knowledge beyond the known chemistry. Quantum chemical treatment can be performed on any kind of real or fictitious compounds, including those that - by any means - cannot even be synthesized. Therefore care must be taken that calculations do have at least a bit of real world basis. In the next sections I have tried to consider such compounds that follow this line of reasoning.

4.3.1 Modification of Salen by Metals Rh and Ir

Not necessarily the cheapest - but the most obvious solution to create a new carrier is the exchange of cobalt against rhodium and iridium. In spite of their exotic nature, such compounds are known and were already synthesised [234]. As mentioned in the first section of this chapter, in numerical assessment of vibrations Co-Salen-oxygen complex energy calculations do not converge without usage of proximal base in this compound class. The same behaviour also shows Rh-Salen. Interestingly, however, in Ir-Salen convergence for both structure optimisation and frequency calculations is obtained without proximal base.

Whereas the Co-Salen reaction shows a reaction enthalpy of -76,15 kJ/mol, Rh-Salen and Ir-Salen are slightly less reactive, -69,30 kJ/mol and -58,99 kJ/mol, respectively. The central atom exchange is obviously disadvantageous.

Alternative ligand development for oxygen carriers As central metals in oxygen carriers, many transition complexes practically come in question. We have treated here only cobalt, but e.g. not manganese, iron or other. This work still remains to be done. In cobalt complexes, one should pursue further development of suitable ligands in order to prevent dimerisation. These all ligands have to coordinate 5 positions in quadratic pyramidal arrangement, leaving the sixth position (almost) free for oxygen. Preliminary calculations, which I will not report in more depth here, with a modified chelate EDTA (ethylendiaminetetraaceticacid), where one carboxy group is exchanged for hydroxy group, have shown such behavior. Another ligands might be from glyoximate family. However, before one starts with the calculation, at least a hint of experimental evidence would be useful to proceed with speculative reasoning.
4.3.2 Quantum Chemical Treatment of Group (VI)-rhenates

In those cases, where the minima on the potential energy surface are unambiguous, the correspondent frequency calculations may be left out. One can then compare the relative reactivity or differences in the reaction energetics of chosen compounds. Here, only the electronic energies within the Born-Oppenheimer approximation might be sufficient to reveal the reactivity trends.

This approach was used in the extensive energetics calculations of 11 different olefines, which might reversibly bind to the ReS$_4^-$ [235], yet another transition metal sulfur coordinated compound. The study was extended towards the ReO$_4^-$ and the ReSe$_4^-$, where the later was suggested to show a more favorable olefin binding ability and therefore could be used as a carrier$^{15}$. Mixed compounds of the form ReO$_i$S$_j$Se$_k^-$ were not considered, since their syntheses are likely not to be feasible at all. Figure 4.21 shows the structures of adducts under examination.

Before I turn to the evaluation of energetics comparison, it has to be pointed out that all species are isoelectronic with OsO$_4$. OsO$_4$ is known as strong, irreversible and selective oxidising agent reacting with double bonds yielding vicinal hydroxides. The exact mechanism of this reaction was long a subject of controversy [236], but according to my knowledge and experience as well as to newer reports it is a concerted [3+2] cycloaddition. In one article [237], authors report that the calculations on this and related compounds can be brought to convergence only by applying DFT with Slater type orbitals (STO). I was able to show that convergence, in particular for transition state, can be achieved by Gaussian type orbitals (GTO) - not only on DFT but also on more conservative HF level. The comparative results with Gaussian software (quite large 6-311+G(d,p) basis set was used) are shown in Tab. 4.10, where, in addition to fully evaluated thermochemistry at 298,15 K, the respective imaginary frequencies for transition states are included.

It is known that HF method is only to be taken as a reference for confirmation of geometries and is of no value when referring to energetics. DFT reveal a clear trend that OsO$_4$ is one order of magnitude more reactive than ReS$_4^-$. Furthermore, the activation barrier

$^{15}$The increase in reactivity should be due to the „trends” in periodic system.
Table 4.10: Reaction of ethylene with three selected isoelectronic compounds: a comparison of quantities

<table>
<thead>
<tr>
<th>compound</th>
<th>OsO₄</th>
<th>ReS₄⁻</th>
<th>ReSe₄⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>method</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3LYP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta_r H_{\text{zero}}$ [kJ/mol]</td>
<td>-154,3</td>
<td>-21,2</td>
<td>-6,84</td>
</tr>
<tr>
<td>$\Delta_r H_{298,15}$ [kJ/mol]</td>
<td>-140,0</td>
<td>-12,7</td>
<td>-0,34</td>
</tr>
<tr>
<td>$\Delta_r G_{298,15}$ [kJ/mol]</td>
<td>-84,4</td>
<td>42,4</td>
<td>53,7</td>
</tr>
<tr>
<td>$E_A$ [kJ/mol]</td>
<td>9,36</td>
<td>35,65</td>
<td>-0,15</td>
</tr>
<tr>
<td>$\omega$ [cm⁻¹]</td>
<td>-284,056</td>
<td>-292,049</td>
<td>-119,943</td>
</tr>
<tr>
<td>HF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta_r H_{\text{zero}}$ [kJ/mol]</td>
<td>-425,5</td>
<td>-166,4</td>
<td>-131,78</td>
</tr>
<tr>
<td>$\Delta_r H_{298,15}$ [kJ/mol]</td>
<td>-408,0</td>
<td>-155,1</td>
<td>-122,5</td>
</tr>
<tr>
<td>$\Delta_r G_{298,15}$ [kJ/mol]</td>
<td>-352,3</td>
<td>-100,3</td>
<td>-68,2</td>
</tr>
<tr>
<td>$E_A$ [kJ/mol]</td>
<td>46,46</td>
<td>74,41</td>
<td>-110,85</td>
</tr>
<tr>
<td>$\omega$ [cm⁻¹]</td>
<td>-535,4</td>
<td>-502,42</td>
<td>-189,423</td>
</tr>
</tbody>
</table>

for OsO$_4$ is four times smaller than the one for ReS$_4$⁻, thus favoring the reaction kinetics. Interestingly, negative activation energy for ReSe$_4$⁻ was found, which might be favourable. The reactivity of ReSe$_4$⁻, however, is about four times smaller than that of ReS$_4$⁻. It can be expected that the reaction would only take place at very low temperatures for obtaining reasonable yields.

In Fig.4.22, the reaction energies (corresponding to approximate values of $\Delta_r H$) for interaction of different olefines with group (VI) rhenates can be found. Reaction enthalpy values obtained by four software packages differ strongly, although comparable functionals, quality of basis sets and general settings were used. In Spartan (BP, 6-31G(d)), in spite of great efforts (e.g. increasing SCF convergence cycle number, turning acceleration DIIS option off, importing already converged solutions from Gaussian, etc.), not all calculations did converge. However, results, where obtained, do well correspond to those in Gaussian (B3LYP, 6-311+G(d,p)) and in Turbomole (BP, def-TZVP). DMol$^3$ again shows unrealistically exothermic reactions.

"What is supposed to be the truth here?" is now the legitimate question. In all calculations, one can see that the reaction with thio-based compounds achieves a maximum in reactivity and seleno-based compounds do not represent any advantages. The oxide anion that is commercially available does not react with olefines at all, for which exists experimental evidence. By QM methods that are fast enough for routine use, no further information can be gained beyond these very qualitative statements.

Conclusion: The speculation that ReSe$_4$⁻ displays more favourable reactivity for olefin binding than ReS$_4$⁻ could be shown to be wrong. The synthesis of the compound should not even be attempted$^{16}$. However, further activation of ReS$_4$⁻ could be perhaps achieved by applying the suitable cation. There exists even the possibility that with an appropriately chosen cation, the pure substance might be liquid itself.

$^{16}$For mechanistic details one should refer to further references, e.g. [238]
Figure 4.22: Comparison charts for enthalpy of reaction by group (VI) rhenates with olefines a) Spartan b) Gaussian c) Turbomole d) DMol³

### 4.3.3 Ionic liquids as carriers?

Ionic liquids can not only be used as solvents for carriers in the membrane phase but can also act as carrier themselves [239]. For olefin separations, in ionic liquid [BMIM][CuCl₂] the anion [CuCl₂]⁻ could, in principle, undergo a reversible reaction with either ethylene or propylene. Studies on DFT (B3LYP) and MP2 level with basis set 6-31+G(d) have clearly given all the stationary points and revealed the reaction path as shown in Fig. 4.23. Using HF procedure, not all calculations did yield the adduct. By this redundant method, however, transition states were not obtained. This is surprising due to the clear MP2 results.

The reaction has be found to be endothermic in all calculations (\(\Delta H_r\) for ethylene DFT: 19 kJ/mol and for propylene DFT: 20,7 kJ/mol; MP2: 29,9 kJ/mol), and will, because of the negative entropy contribution, under no circumstances take place spontaneously (\(\Delta G_r\) for ethylene DFT: 46,3 kJ/mol and propylene DFT: 55 kJ/mol; MP2: 115,8 kJ/mol), in spite of relatively low energy barriers 18,4 and 29 kJ/mol.

The study is further extended to related species: [CuF₂]⁻, [CuBr₂]⁻ and [CuI₂]⁻ in hope that one of the reactions turns out to be exothermal. The results are gathered in Tab. 4.11. Method RHF, 6-31+G* (with ECP LACVP+) was used in Spartan, BLYP functional
4.3. COMPUTATIONALLY DESIGNED CARRIERS

Figure 4.23: DFT energy vs. reaction coordinate: \([\text{CuCl}_2^-]\) with ethylene and propylene. Right: structures and imaginary frequencies for the transition state

with DNP basis set was used in DMol\(^3\), where relativistic effects were taken in the account by the option AER (all electron relativistic), Gaussian was opted by B3LYP functional using 6-311+G(d,p) and LANL2DZ (for iodine) basis set and in Turbomole, B3LYP functional with def-TZVP basis set was used.

Table 4.11: Reaction enthalpies without thermal corrections for ethylene addition to halogencuprate anions \([\text{CuX}_2^-]\)

<table>
<thead>
<tr>
<th>software</th>
<th>fluorine [kJ/mol]</th>
<th>chlorine [kJ/mol]</th>
<th>bromine [kJ/mol]</th>
<th>iodine [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spartan</td>
<td>27.05</td>
<td>13.71</td>
<td>14.72</td>
<td>-</td>
</tr>
<tr>
<td>DMol(^3)</td>
<td>-40.03</td>
<td>-38.64</td>
<td>-44.90</td>
<td>-48.39</td>
</tr>
<tr>
<td>Gaussian</td>
<td>16.34</td>
<td>17.59</td>
<td>16.37</td>
<td>13.65</td>
</tr>
<tr>
<td>Turbomole</td>
<td>15.28</td>
<td>13.14</td>
<td>10.62</td>
<td>7.80</td>
</tr>
</tbody>
</table>

Conclusion: In Spartan, HF calculation on \([\text{CuI}_2^-]\) failed, thus putting in question the reliability of subsequent DFT calculations with this compound, which I discarded from the results table. Except for DMol\(^3\), the results are consistent within Gaussian and Turbomole: it could be shown that in all cases the reactions are endothermic. The reaction energies are within the narrow window around 12 kJ/mol. The synthesis of the compounds should not be attempted for the purpose of olefine separation, since the distortion of linear \([\text{CuX}_2^-]\) molecules seems to be unfavourable. The liquids can merely be used as solvents.

4.3.4 Dicationic Olefin Ni(II), Pd(II) and Pt(II) Complexes

Here, I have chosen a class of a compounds that was already synthesized [240]. One might argue about the ligand’s costs, but surely the more expensive pyridine based ligand
can be exchanged for some other more affordable ligand source (e.g. acridine \[241\]).

This chosen carrier (Fig. 4.24a) is also a catalyst for a variety of reactions. Its structure reminds of Zeise’s salt. However, apart from being pro-quadratic planar ligand, it is also a dication. As we have seen above, negatively charged ions (like \( \text{CuCl}_2^- \)) will hardly interact with the electron rich double bond of the olefine. Thus, a cation must be in this form highly electrophilic. The course of addition reaction is shown in Fig. 4.24b. As in the case of Ag(I), Cu(I) and Co-Salen, this reaction shows no obvious transition state. Furthermore, nickel can be used as a central atom instead of more precious palladium or platinum for which ligand provides rigid tridentate planar environment.

Figure 4.24: DFT energy vs. reaction coordinate for ethylene-dicationic olefin complexes (\( M = \text{Ni, Pd, Pt} \)): reaction coordinate is approximated by ethylene ligand to metal distance

For comparison, again two software packages were used. The reaction enthalpies, gathered in the Table 4.12 show consistent behaviour and the values are sufficiently high thus promising a starting point for a carrier development.

Table 4.12: Reaction enthalpies without thermal corrections for ethylene addition to dicationic cation

<table>
<thead>
<tr>
<th>software</th>
<th>nickel [kJ/mol]</th>
<th>palladium [kJ/mol]</th>
<th>platinum [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMol³ (BLYP, DFT-SCP, DNP)</td>
<td>-175.7</td>
<td>-181.3</td>
<td>-229.1</td>
</tr>
<tr>
<td>Turbomole (BP, RI, def-TZVP)</td>
<td>-148.5</td>
<td>-153.0</td>
<td>-195.7</td>
</tr>
</tbody>
</table>

Further interesting compounds based on five coordinated platinum (II) that are closely related to Zeise’s salt were reported, where a variety of ligands was proposed \[242, 243\].

Even more exotic potential carriers might be those on titanium basis. Here, cycloaddition reactions with alkenes and alkynes were observed \[244\]. Surely interesting are also

\(^{17}\)Experimentally, meta position is activated for alkylation in pyridine. Therefore, the desired ortho product can not be obtained by direct synthesis. In acridine, this is more easily achieved.
4.3. COMPUTATIONALLY DESIGNED CARRIERS

Hydridotrihalostannato complexes of platinum [245]. The problem with these compounds is that the reaction occurs only at low temperatures (mostly between -50°C and -80°C) and is not always reversible. More promising for applications at ambient and technical conditions are aluminium \(\beta\)-diketinimate complexes, where reversible ethylene cycloaddition was reported [246]. However, the very nature of this compounds may be yet another starting point for further research.

4.3.5 Carriers for carbon dioxide

The mechanism of reactive absorption of CO\(_2\) into aqueous solutions of industrially used amines (e.g. monoethanolamine, etc.) is still not known [73]. Two mechanisms have been postulated so far: zwitterion sequential and trimolecular synchronous mechanism. In the following reaction equations

\[
\begin{align*}
\text{CO}_2 + \text{R-NH}_2 & \rightleftharpoons \text{R-NH}_2^+ - \text{COO}^- \\
\text{R-NH}_2^+ - \text{COO}^- + \text{H}_2\text{O} & \rightleftharpoons \text{R-NH-COO}^- + \text{H}_3\text{O}^+,
\end{align*}
\]

the question to be answered is, whether the two steps take place simultaneously or not. Quantum mechanical methods cannot provide the assessment of all individual steps of the postulated reaction course, where also equilibria of water dissociation and its pH value due to the presence of amine as well as CO\(_2\) partial pressure play a significant role.

Interestingly however, when treating the reaction of interest in a gas phase with a variety of methods (HF, MP2, DFT), there is almost no interaction between carbon dioxide and amine functionality. Merely at semiempirical level one obtains intuitively reasonable structure for the addition product, the carbamate. Continuous solvation models can only be used for the reactants and products in order to obtain satisfying results. The transition state search using these methods ends with non-closed cavity problem, where the proton jump seems to cause the solute cavity to fall apart and its bonding to adjacent atoms is not sufficiently defined anymore. Therefore, I have used an explicit solvent approach, where unfortunately, energetics of the reaction cannot be unambiguously evaluated. The initial arrangement of the reactants, which is of course not dependent on the postulated mechanism (without solvent water molecules) can be seen in Fig. 4.25a.

Procedure: Semiempirically (AM1) determined structure of zwitterion was put into a box of solvent (model water, PBC). Subsequently, ab-initio (HF, 6-31G**) calculation was performed in order to establish the geometry of the system at its lowest energy. In the energy minimum, the zwitterion remains stable Fig. 4.25b, i.e. one does not automatically obtain an organic anion and hydronium-ion. From here on, the bond length between the C-atom of the carbon dioxide and N-atom of amine was artificially prolonged step-wise by applying constrained optimisation. Looking at the electron density represented by the contour plots in Fig. 4.25b and c, the proton transfer from the hydronium ion to the nitrogen atom takes place at C-N distance between 1.45 Å and 1.5 Å. The bond of nitrogen atom to CO\(_2\) is, however, at the same time not yet broken. Amine is fully rebuilt by leaving CO\(_2\) group at C-N distance of 2.05 Å. Therefore, the zwitterion is stable in aqueous environment. This is also true according to DFT/CSM quantum mechanical
4. MOLECULAR MODELLING

Figure 4.25: CO₂ addition to ethanolamine: a) initial structure that holds for both postulated mechanisms b) lowest energy state: products from dissociated zwitterion c) transition state

models. Some energy values for well converged solutions of species involved in the reaction are given in Table 4.13.

Table 4.13: Electronic energies for the species involved in CO₂ absorption by ethanolamine (Gaussian; B3YLP/6-31+g(d)) resp. 6-311++g(d,p), DMol³/DND

<table>
<thead>
<tr>
<th>solvation method</th>
<th>ethanolamine [hartree]</th>
<th>CO₂ [hartree]</th>
<th>H₂O [hartree]</th>
</tr>
</thead>
<tbody>
<tr>
<td>cpcm</td>
<td>-210,4085928</td>
<td>-188,5947900</td>
<td>-76,4376151</td>
</tr>
<tr>
<td>iefpcm</td>
<td>-210,4773002</td>
<td>-188,6512162</td>
<td>-76,4724311</td>
</tr>
<tr>
<td>cosmo</td>
<td>-210,4246451</td>
<td>-188,6560163</td>
<td>-76,4513484</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>solvation method</th>
<th>H₃O⁺ [hartree]</th>
<th>anion [hartree]</th>
<th>zwitterion [hartree]</th>
</tr>
</thead>
<tbody>
<tr>
<td>cpcm</td>
<td>-76,8339624</td>
<td>-398,5554007</td>
<td>-399,0081318</td>
</tr>
<tr>
<td>iefpcm</td>
<td>-76,8726645</td>
<td>-398,6705932</td>
<td>-399,1264023</td>
</tr>
<tr>
<td>cosmo</td>
<td>-76,8622233</td>
<td>-398,6070311</td>
<td>-399,0808005</td>
</tr>
</tbody>
</table>

From these values, where an isolated zwitterion (the proton acceptor, i.e. water molecule is not included) is taken into consideration, reaction energetics can be deduced. Applying CPCM model, the formation of a zwitterion is exothermic (-12.5 kJ/mol) and subsequent step, where the zwitterion reacts with water, is endothermic (148 kJ/mol). With IEF-PCM model, zwitterion formation is slightly endothermic (5.5 kJ/mol) and the ion formation endothermic (145.8 kJ/mol). In COSMO run, respective values are -0.4 kJ/mol and 165.1 kJ/mol.

To my opinion, the sequential zwitterion mechanism is more plausible, since:

- both the formation of a zwitterion from amine and CO₂ and
- the formation of a zwitterion from ionic species are highly favored,
- the proton jump occurs at almost fully intact carbamide bond, as can be seen from the electron density.

Reaction is thus not concerted and occurs in two distinguished steps. One can speculate, whether in the second step, which is a proton transfer, tunnelling effect causes the search for the defined transition state to fail.

### 4.3.6 Other carriers

For further carriers, I would like to refer to the literature.

**Carriers for carbon monoxide:** Carriers for carbon monoxide are usually treated together with silver(I) salts, since double C=C and C=O bonds both coordinate the metal in comparable manner [213]. Metal carbonyl compounds are not suitable as carries for carbon monoxide since the bond is too strong and no ligand exchange can easily take place. This behaviour was not studied in QM level but was proven experimentally [247, 248, 249, 250]. My own DFT studies on carbon monoxide carriers are based on macrocyclic iron (II) complexes [251]. This carrier does show essentially the same features as does Co-Salen.

**Carriers for hydrogen:** Chemisorption of hydrogen on palladium metal is the essential step in hydrogen separation with membranes. This topic was treated quantum mechanically on the level of clusters [252], whereas knowledge on metal surfaces [253] also seems to be important. Introductory study of this system is a part of the tutorial to ADF software [161], available at the respective home-page.

**Carriers for water:** When compared to alcohols or ketones, water vapor is preferably transported through silica and zeolite membranes, since it displays much higher affinity to these solids. I have performed some preliminary studies on adsorption of water on amorphous SiO$_2$ clusters. An example of a calculation (total charge of -16 has been considered) is given in Fig. 4.26. Again, no transition state with an obvious barrier could be detected.

### 4.3.7 Solvent effects on solutes solubility

Solvents can be generally characterised by their donor number, which is represented by the measured enthalpy of the reaction of the solvent with the strong Lewis acid BF$_3$ (used especially for aprotic solvents), by their dipole moment (i.e. polarity) and their dielectric constant [127]. It is well known that highly charged solutes, ions, are better stabilised in very polar liquids like water. This classical view can be confirmed by the results presented in Fig. 4.27a, where stabilisation energy is gained by dissolving different molecules in different solvents, represented by their dielectric constant. A non-polar molecule like methane will be less stabilised by being dipped into polar solvents than more polar molecules (stabilisation increases from CO$_2$ over methanol to water). The non-polar solute’s absolute energy, which depends on the geometry, will change only slightly
when dissolved in a non-polar solvent. The stabilisation energy, furthermore, in general increases with increasing dielectric constant for all molecules (the sum of dispersion forces will be increased due to the presence of more polar solvent, while the solute remains almost unchanged). Singly charged ions, positive as well as negative, will be almost equally stabilised with solvation energy release up to 200 kJ/mol. Common (inorganic) ions show stabilisation energies comparable to those of ionic liquid’s ions. Ionic compounds, however, do not consist of single ions, therefore ionic pairs must be considered as a first approximation\textsuperscript{18}. The extent of further self-aggregation cannot be accounted for with existing models.

Figure 4.26: Model SiO\textsubscript{2} cluster and addition of water to its surface: a) geometry (coordination is denoted by thin-lined bonds) b) energy vs. reaction path when dissolved in a non-polar solvent. The stabilisation energy, furthermore, in general increases with increasing dielectric constant for all molecules (the sum of dispersion forces will be increased due to the presence of more polar solvent, while the solute remains almost unchanged). Singly charged ions, positive as well as negative, will be almost equally stabilised with solvation energy release up to 200 kJ/mol. Common (inorganic) ions show stabilisation energies comparable to those of ionic liquid’s ions. Ionic compounds, however, do not consist of single ions, therefore ionic pairs must be considered as a first approximation\textsuperscript{18}. The extent of further self-aggregation cannot be accounted for with existing models.

Figure 4.27: Calculated solvation energies for different molecules and their dependance of dielectric constant: a) Gaussian IEFPCM model b) Turbomole COSMO model. Zero energy corresponds to the energy of molecules geometry in vacuum $\epsilon = 1$.

\textsuperscript{18}Pairwise interactions of ionic liquid’s anion and cation that determine their mutual orientation are difficult to examine. Orientational degrees of freedom that can be encountered are infinite and only local minima can be obtained.
4.3. COMPUTATIONALLY DESIGNED CARRIERS

Basically, the same stabilisation trend can be observed in Fig. 4.27b, where different software was used and different solvation model was taken. For methane, carbon dioxide, methanol, water, [BTA]⁻ and [BMIM]⁺ results are consistent, although the stabilisation energies are different. Data for some additional compounds, including ion pairs of ionic liquids, were calculated: IL1 and IL2 denote a neutral charged ionic liquids at two different geometries (presented in Fig. 4.28a), each consisting of one cation ([BMIM]⁺) and one anion ([BTA]⁻). IL21 and IL22 represent ionic liquids composed of two cations and two anions, also at two different geometries. Anions BF₄⁻ and HgI₂⁻ are also represented and will be, according to their charges, highly stabilised in polar solvents.

It can be seen from the Fig. 4.27b that all neutral ionic liquids (ionic pairs) are much more polarisable than water! This means that they must provide very „soft” electronic environment in order to be polarised by external medium. Under „soft” electronic environment one understands charged species with highly delocalised electrons providing the means for dispersion (van der Waals and London) force interactions. In case of ionic liquids, their ionic nature does not lead to high electrostatic forces known from ionic crystals and that is the reason that they are liquid at room temperature.

Furthermore, ionic liquids as solvents do not follow the classical rules on solubility, which is expressed by alchemists „similar dissolves in similar”. According to this heuristic rule, ionic compounds like inorganic salts should have been highly soluble in these solvents, which is not true. Rather a new concept is needed to approach the characterisation of ionic liquids in the respect of their solvation capacity. Following a polarised continuum solvation models (PCM), ionic liquids - as every other solvent medium - must be represented by dielectric constant, which I have measured in an experimental part of this work. However, apart from the lack of reliable values for the dielectric constant [254], the concept of this representation do not work completely satisfying.

One approach to attack this problem is the usage of „similar polarisation principle”, just in the same manner as this is known from Pearson’s soft and hard acid and basis (HSAB) concept [255]. Whereas HSAB concept is hardly quantifiable, I propose here to provide a quantification method by means of quantum mechanics. In Fig. 4.28b typical output for solvation results from Gaussian software is presented.

Figure 4.28: Two different ionic liquid structures, i.e. ion pair [BMIM]⁺ [BTA]⁻ a) IL1 b) IL2 c) PCM results from Gaussian output
In the output file we should focus on „dispersion energy” that might be used as a quantity in evaluation of the compound’s „softness” and on (solute)-solvent energy, which denotes the stabilisation of the medium through dissolved solute. In Table 4.14 dispersion energies for several compounds are included. These energies are proportional to the solutes surface\(^{19}\). Cavitation energy is the energy required for the solvent to make the cavity for the solute and it increases with the molecules volume. Repulsion energies are included for the sake of completeness, electrostatic energies omitted.

### Table 4.14: Information about solvation effects in Gaussian output for several compounds (IEF-PCM)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>IL1</td>
<td>149,41</td>
<td>-102,30</td>
<td>5,73</td>
<td>-134,85</td>
</tr>
<tr>
<td>IL2</td>
<td>148,82</td>
<td>-103,30</td>
<td>5,69</td>
<td>-114,52</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>41,76</td>
<td>-12,89</td>
<td>0,25</td>
<td>-0,25</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>23,68</td>
<td>-16,36</td>
<td>2,05</td>
<td>-36,27</td>
</tr>
<tr>
<td>CH(_3)OH</td>
<td>39,92</td>
<td>-21,92</td>
<td>1,55</td>
<td>-26,40</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>33,76</td>
<td>-22,68</td>
<td>2,30</td>
<td>-10,38</td>
</tr>
<tr>
<td>(CH(_3))(_2)CO</td>
<td>59,83</td>
<td>-30,75</td>
<td>1,30</td>
<td>-20,67</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>48,03</td>
<td>-39,75</td>
<td>3,97</td>
<td>-14,52</td>
</tr>
<tr>
<td>benzene</td>
<td>59,50</td>
<td>-47,32</td>
<td>4,35</td>
<td>-15,69</td>
</tr>
<tr>
<td>NaCl</td>
<td>35,19</td>
<td>-23,01</td>
<td>2,89</td>
<td>-263,13</td>
</tr>
<tr>
<td>CuCF(_3)COO</td>
<td>66,44</td>
<td>-38,66</td>
<td>3,10</td>
<td>-81,59</td>
</tr>
<tr>
<td>CuAlCl(_4)</td>
<td>74,48</td>
<td>-53,76</td>
<td>6,57</td>
<td>-194,85</td>
</tr>
<tr>
<td>CuBiLCl</td>
<td>169,00</td>
<td>-98,91</td>
<td>5,44</td>
<td>-96,36</td>
</tr>
</tbody>
</table>

For example, ionic liquids generally show complete miscibility with CH\(_2\)Cl\(_2\) or toluene or even acetone, all displaying high dispersion interactions. On the other hand, many ionic liquids are immiscible with water or methanol. Results from the table do confirm this trends.

Looking at the inorganic salts however, clear statements are not possible. Although both NaCl and CuAlCl\(_4\) are very „hard” they show comparably high dispersion energies and extremely high (solute)-solvent energies. Softer Cu\(^+\)CF\(_3\)COO\(^-\) and CuBiLCl (copper phenanthroline compound treated above) do experimentally dissolve better. Here, it seems that both dispersion energies and (solute)-solvent energies must lie as close to those of ionic liquids as possible.

It can be concluded, that when organic compound and ionic liquid are mixed together, one can expect better solubilities in cases when the dispersion energy of the organic compounds is as high as possible and ideally lies in the same order of magnitude as that of the ionic liquid. This proposed concept unfortunately does not apply to inorganic compounds. Currently, the interpretation I provided seems to be the only reasonable one, since no solvation model exists, which would be able to describe aggregated charged

\(^{19}\)This explains why small molecule like hydrogen is not well soluble in liquids.
4.4. PROCESS PARAMETERS FROM MOLECULAR MODELLING

Chemical properties, in particular the reactivity, i.e. the reaction thermodynamics, and the reaction mechanisms of potential carriers, were treated in the sections above. Tools from the field of molecular modelling can further provide process related parameters needed for quantification of mass transport through the liquid membranes: gas-liquid equilibria data and diffusion coefficients.

4.4.1 Calculations of gas and vapour solubilities in ionic liquids

COSMOtherm method does not allow for direct gas-liquid equilibrium calculation superimposed on chemical reaction. However, it can be used for calculation of (physical) gas and vapour solubilities in ionic liquids with supposedly higher precision than the „usual“ group contribution methods [116]. Ideally, these solubilities are expressed according to Henry’s law in term of temperature dependent Henry coefficients:

\[ p_i(T) = H_i(T) \cdot x_i, \]

where \( p_i \) is the equilibrium pressure of selected compound \( i \). The composition of the chosen liquid is expressed as the molar fraction \( x_i \). In the following, I have used automatical calculation of Henry coefficients using \text{Henry}=1 \text{ xh=\{0.5 0.5\}} command route for ionic liquids based on gas phase energies, \( \sigma \) profiles and possibly on developed QSP relationships. Alternatively, iterative procedure is possible by postulating the chemical potential equilibrium equations with activity coefficients for a biphasic system, but this approach was not followed here.

Prerequisite calculations for COSMOtherm method include geometry optimisation of all the molecules under consideration. These are the ionic liquid’s cations and anions, gases and vapours. Quantum mechanical treatment is performed with Turbomole program on DFT level using Becke-Perdew (BP) GGA functional with def-TZVP basis set and RI approximation for which COSMOtherm is parameterised.

Here, two ionic liquids [BMIM]\(^+\) [BTA]\(^-\) and [BMIM]\(^+\) [CuCl\(_2\)]\(^-\), that are later also used in experiments, are considered. Conformational analysis of cation [BMIM]\(^+\) is sufficiently

\(^{20}\)Solubility of solids in different solvents can also be calculated by the program COSMOtherm automatically in a black box procedure, where pure electrostatic interactions are not taken into account sufficiently. In ionic liquid [BMIM]\(^+\) [BTA]\(^-\), following solubilities for NaCl, CuBiLCl, CuAlCl\(_4\) and CuCF\(_3\)COO were obtained (expressed in mol fractions): 0.000287, 0.0333, 0.493 and 1.0 (!), where according to this data the latter compound should completely dissolve in the liquid ionit.
4. MOLECULAR MODELLING

accurately performed with molecular mechanics (MMFF force field), conformations of anion \([\text{BTA}]^-\) are determined with semiempirical method AM1. Although the cation forms 27 different conformers, inclusion of them all does not contribute significantly to the accuracy of the COSMO\textit{therm} calculations, where compounds are statistically weighted according to their energy levels (Boltzmann distribution). However, once cosmo-files are calculated, they can remain included since the calculational costs are negligible. On the other hand, non-parameterised COSMO-radii \(^{21}\) of elements, particularly in case of the presence of transition metals in any of the compounds, greatly influence the outcome of the calculation.

**Permanent gases**

Calculated Henry coefficients for selected permanent gases and vapours at different temperatures are gathered in Fig. 4.29. In the temperature range of interest i.e. between room temperature and 200°C, one can see that with increasing temperature the solubility decreases.

![Figure 4.29: Calculated Henry coefficients in ionic liquid \([\text{BMIM}]^+ [\text{BTA}]^-\) for selected permanent gases and vapours](image)

Experimentally it was found that hydrogen is not very soluble in ionic liquid and the calculation does confirm this finding. The difficulty with oxygen and nitrogen is that the calculated Henry coefficients and their ratios do not correspond with experimental trends: there is almost no difference in solubilities of these two gases by COSMO\textit{therm} methods. Compiled literature data \(^{256}\) show that oxygen, as a rule of the thumb, is twice as soluble in arbitrary liquid as nitrogen. The cause for the discrepancy lies in

\(^{21}\)Through the Turbomole subroutine cosmoprep one finds out that cosmo radius, where electrostatic charges are mapped on, is only available for H, C, N, O, S, F, Cl, Br and I atoms. For all other atoms, no optimised radius is available and so called bondii radius multiplied with the factor 1.17 is recommended to be taken instead. If needed, bondii radius can be calculated separately from isodensity surfaces. For the approximate values, van-der Waals radii can be taken, but for exact values one has to use experimental results. DMol\(^3\) program that is also parameterised for COSMO\textit{therm} method is in this case not a superior tool.
the poor resolution of surface segment charges in the course of cosmo PCM calculation [257], although triplet ground state was assumed for oxygen. For other di- and three-atomic molecules the surface charges are better defined and the results reflect at least the solubility trends. For instance, methane and carbon dioxide both dissolve well in ionic liquid but to different extent. This effect also was reproduced experimentally. It was shown that different solubilities of hydrogen methane and carbon dioxide as they are important components of natural gas can be of an advantage in membrane separations [258].

Solubility of nitrous gases is comparable to those of carbon monoxide and methane. Very interesting behaviour shows ammonia, which is a strong base and hydrogen sulfide, which is a strong acid: the solubility curves lie very close to each other. Water and sulfur dioxide show the highest solubility of all compounds treated so far. In practice, however, [BMIM]$^+$ [BTA]$^-$ is not almost miscible with water (max. 1 wt.%). It has to be noted that ammonia as a strong base irreversibly reacts with imidazoliium-based ionic liquids in position 2 (carbene product is built by subtraction of hydrogen unless the position 2 is blocked by methyl functionality).

**Different C1-C4 Hydrocarbon Vapours**

Temperature dependent Henry coefficients for representative C1-C4 hydrocarbon compounds in two ionic liquids, namely [BMIM]$^+$ [BTA]$^-$ and [BMIM]$^+$ [CuCl$_2$]$^-$ can be found in Fig. 4.30. The values are calculated for the temperatures up to 200°C, where the solubilities decrease with increasing temperature.

![Figure 4.30: Calculated Henry coefficients for different lower hydrocarbons in ionic liquids](image)

It can be clearly seen that solubilities increase with increasing chain length - this is reasonable, since the decreasing vapor pressures of the compounds play an important role (and are considered in the calculation by their electronic gas phase energies). Furthermore, unsaturated hydrocarbons show about two times higher solubilities that their saturated counterparts, which also seems to be a general property, independent of the solvent used.
Now, computational evidence was provided for the influence of the anion choice on the solubility. In experimental section of the thesis it will be shown, whether these trends are in agreement with measurements.

4.4.2 Diffusion coefficients in ionic liquids

As seen in the introduction, the major mechanism of transport in liquid membranes is diffusion. Therefore, the knowledge of diffusion coefficients is essential for accurate description of the liquid membrane system’s performance. Having in mind the basic mechanism of molecular diffusion, where the mass transport takes place by spatial pairwise exchange of molecules, all transported species must be included in consideration \([136, 138]\). In case of binary feed mixture entering a membrane module and further the membrane material, these species are: the two pure permeants, the carrier, the carrier complex and finally, the liquid phase species. For method evaluation purposes, diffusivities of propane and propylene only are considered within the computational study. The liquid phase is formed by ionic liquid consisting of cations \([\text{BMIM}]^+\) and anions \([\text{BTA}]^-\). The diffusivities of the carrier and the carrier complex with propylene in this ionic liquid are calculated separately with group contribution method (see Chapter 3).

Both, „how to do“ and the simulation itself are described in the following sections. Some introduction is given first. However, for reasonable setting of all the simulation parameters, more profound theoretical background is required, which is provided in the literature \([259, 260]\).

Simulation background

Theoretically, statistical mechanics provides a means for determining physical properties that are associated with more than one molecule at more than one geometry, i.e. with a molecular ensemble. Here, a three dimensional sample of periodic, meso- or macroscopic bulk (liquid) is dealt with, where the net result of the interactions of many molecules in many conformations with different properties and, if applicable, in different energy states is evaluated.

Molecular dynamics (MD) simulation, i.e. the simulation of the time-dependent behavior of a molecular system, is the generic term of methods for obtaining information on the physical properties of ensembles.

In practice, the difficult part of this process is not the calculation and evaluation of statistical mechanics, but obtaining all the information about the possible conformations, energy levels and predominantly, about the adequate description of the molecular interactions. These interactions are usually defined by so called (parameterised) force fields included in an energy expression for the particular system. In the energy expression, the atoms in the molecules are considered as simple mass points, connected by stretch, bend and torsion springs. Intra- and intermolecular interactions comprise van-der-Waals (usually expressed by Lennard-Jones 12-6 function) and electrostatic parameters. Advanced force fields also include molecular (e.g. dipole, quadrupole and higher) moments. The
most general force field type are the Universal Force Fields (UFF). The energy expression is used to compute the forces on the atoms for any given geometry at certain temperatures and pressures. The application of molecular dynamics to liquids or solvent-solute systems allows the computation of properties such as (self) diffusion coefficients resulting from cumulative vibrational and Brownian motion. It is important to notice that one cannot just pick up a force field from the large scope of force fields available today. The usage of UFF must be always taken with caution, especially in case of ionic liquids, for which no special parametrisation has been performed so far.

The difficulty in molecular dynamics simulation for determination of diffusion coefficients in ionic liquids is to take account for the long range electrostatic interactions. These interactions, which, in contrast to the short range of Lennard-Jones potential \( \frac{1}{r^{12}} + \frac{1}{r^{6}} \), decrease inversely proportional with the distance \( r \) of the two selected points \( \frac{1}{r^2} \). Therefore, a spatially bigger initial sample (with more molecules included) must be included in the MD study.

Many freely available and commercial MD tools are available on the market (e.g. GROMACS, Tinker, GULP, Sybyl Dynamics, VASP/VAMP, MOE - to mention only a few). They usually include several different force fields that are each parameterised for a specific application. In this work, the demonstration version of Discover, a molecular mechanics/dynamics program integrated in Materials Studio, is used. The main goal is the evaluation of the reliability and applicability of the MD tool for engineering purposes in the following case study. Comparable work was extensively performed on polymer materials, in particular in the field of membrane separation, among it e.g. [93, 94, 112].

**MD case study**

The ideal behavior for the case study system (propylene/propane/IL) is assumed throughout the study, for which no interactions between propane and propylene take place. Therefore, two distinctive systems are examined in the same manner: firstly, propylene/ionic liquid and secondly, propane/ionic liquid.

Molecular dynamics simulation of an (equilibrium) system can be comprised in the following steps:

1. **Setting up initial structures:** The first stage is the geometry generation of the molecules involved in the system. After assigning a chosen force field, their geometry is individually optimized by molecular mechanics in order to obtain stable conformations. The following separate quantum mechanical treatment is optional for assignment of (electrostatic) atomic charges to the individual atoms. If applicable, now another force field can be used (applying calculated atomic charges). The obtained structures (propylene, [BMIM]$$^+$$, [BTA]$$^-$$ and propane, [BMIM]$$^+$$, [BTA]$$^-$$ respectively) are now used to create a 3-D periodic cell.

2. **Building of an (amorphous) periodic cell:** A liquid of certain density is simulated by putting a number of molecules into a specific volume. The form of the volume is usually chosen as a cube, but might also be a hexagon or a cylinder. In order to reduce computational costs, the system should be as small as possible. However, in small systems,
significant fraction of molecules would be against the wall of the box. To avoid severe edge effects, periodic boundary conditions (PBC) are used to make it appear as though the fluid is infinite. Actually, the molecules at the edge of the next box are a copy of the molecules at the opposite edge of the box. When long range interactions are to be taken into account, the cut-off distance must be appropriately set. Specification of simulation parameters include:

a) The choice of the total quantity of constituent molecules of the cell.

b) The ratio of the solute molecules to the molecules of the bulk liquid.

c) Cut-off distance sufficient to exclude particular interactions (targeting e.g. infinite dilution).

d) The temperature, the pressure and the density of the system. They determine the lattice parameters of the cell.

Total number of molecules is targeted between 80-100. The approximate ratio of the solute to the bulk liquid is specified according to experimental data (1:10), however, an infinite dilution for propane-propane and propylene-propylene interactions, respectively, is aimed at here, too. It is assumed that at an average cut-off distance of 10 Ångstrom between each propane/propylene molecule is sufficient enough to exclude interactions. A cubic cell with one propene/propane molecule is filled up with an ionic pair \([\text{BMIM}]^+ [\text{BTA}]^-\) until a side length of 10 Ångstrom is reached. The obtained cube is then scaled using the rule of the thumb by factor 2.5 yielding a cell of 26 Ångstrom side length. The number of the molecules in the cell then determine the ratio. Subsequently, all the molecule types are multiplied with the same factor until the desired total number of molecules is reached.

It was assumed as reasonable that the propylene/propane fraction does not affect the density of the system. Therefore, the solute concentration independent (experimental) density of the ionic liquid was considered. Since the analysed system is non-compressible and the application is run near ambient conditions, the temperature is set to 298.15 K and the pressure to 1 bar.

Some configuration details of the amorphous cells used in the case study are given in Table 4.15:

After all parameters have been set up, „unrelaxed“ cubic cell is generated using random algorithm, where molecules may not be equally distributed throughout the cell, thus creating vacuum cavities.

3. Relaxing the cell: An energy minimization and subsequent molecular dynamics (pre)-simulation on molecular mechanics level is performed in order to correct the vacuum voids, to condense the matter and to equilibrate the liquid phase in the cell. This procedure should be carried out whenever an amorphous cell is constructed. In preferences, an appropriate force field must be chosen first - the one that will be applied later in the production run. Such (parameterised) force field that is capable to handle the ionic liquid is e.g. Consistent Valence Force Field (CVFF). In order to accurately account for non-bond parameters, both van der Waals & Coulomb options must be set. In this work,
Table 4.15: Configuration data for the cell construction

<table>
<thead>
<tr>
<th>System Propylene - Ionic Liquid</th>
<th>Propane</th>
<th>[BMIM]$^+$</th>
<th>[BTA]$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of molecules</td>
<td>4</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Total number of atoms</td>
<td></td>
<td>1636</td>
<td></td>
</tr>
<tr>
<td>Total cell density</td>
<td></td>
<td>1470 kg/m$^3$</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td>298.15 K</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>System Propane - Ionic Liquid</th>
<th>Propane</th>
<th>[BMIM]$^+$</th>
<th>[BTA]$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of molecules</td>
<td>4</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Total number of atoms</td>
<td></td>
<td>1644</td>
<td></td>
</tr>
<tr>
<td>Total cell density</td>
<td></td>
<td>1470 kg/m$^3$</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td>298.15 K</td>
<td></td>
</tr>
</tbody>
</table>

Charges on atoms or functional groups are calculated automatically\(^{22}\).

Analogous to the previous molecular mechanics minimization of the individual constituent molecules, now the \(\text{steric}\) energy of the cell ensemble is to be brought to a minimum according to the adjusted convergence level. After the job's completion, minimised structure of the cell is obtained.

The subsequent step called \(\text{equilibrating a cell}\) includes relatively short molecular dynamics (pre)simulation, performed within NPT ensemble. N stands for constant number of moles, P for constant pressure, and T for constant temperature. In addition to the choice of ensemble, the temperature, the pressure, and the time-related control settings of the dynamics simulation must be specified:

a) The time duration for each dynamics step is crucially important for the outcome of the simulation. Too large time step will cause atoms to move too far along a given trajectory, thus poorly simulating the motion and resulting in inaccuracy and instability. A time step that is too small will make it necessary to run more iterations, thus taking longer to run the simulation. Generally, as a rule of thumb, the time step should be one order of magnitude less than the timescale of the shortest motion. This corresponds to the vibrational period or to the time between collisions. The highest vibrational frequency is that of C-H bond stretching, whose period is in the order of \(10^{-14}\) s, i.e. equivalent to 10 femtoseconds (fs). The integration time step taken in the case study is 1.0 fs.

b) The time of the whole molecular dynamics simulation. It depends on the size of

\(^{22}\)It is necessary to take care that the charges are correctly assigned for cations and anions. However, it could be shown in test runs that supposedly more precise calculation of charges through quantum mechanics do not improve results. The charge assignment must be performed manually on auxiliary files, which supplement structural information.
the system, with larger systems needing longer equilibration periods. The minimum can be considered to be 50 picoseconds (ps); in the case study the dynamics time is set to 100 ps\textsuperscript{23}.

The number of dynamics steps is automatically determined by the length of one step and the length of the dynamics simulation. Time-related settings for (pre)optimisation MD in the case study are summarised in the Table 4.16:

<table>
<thead>
<tr>
<th>Length of dynamics step</th>
<th>1,0 fs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation time</td>
<td>100 ps</td>
</tr>
<tr>
<td>Number of dynamics steps</td>
<td>100000</td>
</tr>
</tbody>
</table>

The trajectory of the individual molecules generated from an equilibration simulation has no value. The final position, however, is the starting point for the production MD simulation run and must be saved. The equilibrated cell structure, shown in Fig. 4.31 is returned after the completion of the job.

Figure 4.31: Cell construction: a) charges assigned to anion and cation b) relaxed and equilibrated cell structure

4. The molecular dynamics production run: Production run does not differ much from the MD run needed for prerequisite equilibration of the cell. Firstly, in order to calculate the diffusion coefficients, the assessment of mean squared displacement of propylene or propane molecules within the cell is required for the duration of the simulation. In each time step the movement of the atoms/molecules is recorded into the individual frame. All frames together build up the full trajectory record, which is subsequently the subject of the analysis.

\textsuperscript{23}Running molecular dynamics simulations is computationally as expensive as working with \textit{ab initio} or DFT calculations. Due to the large amount of information being processed (molecular structures and forces, temperature, pressure, density, boundary conditions) and the large number of iterations needed to obtain a good statistical description of the system.
4.4. PROCESS PARAMETERS FROM MOLECULAR MODELLING

Secondly, NPT thermodynamic ensemble used above is switched to the NVE thermodynamic ensemble. This ensemble works with constant number of moles, constant volume and constant (kinetic and potential) energy. MD with NVE ensemble does not artificially interfere with the thermodynamics of the system as in the case of ensembles using thermostats. Simulation time is doubled (200 ps) in comparison to the equilibration run, step duration still being set to 1.0 fs, the simulation having herewith 200000 dynamics steps.

5. Analysis of the production run: After the completion of the production run, the output file is analyzed in terms of mean squared displacement (MSD) for the respective molecules to be examined\textsuperscript{24}. The commercial Discover Analysis tool automatically generates a graph of MSD for propylene and propane, formerly being selected as targets, over time. These values must however, still be exported to table calculation program in order to be further subjected to analysis. Figure 4.32 illustrates the typical results for a good run (a) and a bad run (b), where in the later the movement of particles is overall very slow. Furthermore, after it reaches a maximum, movement deceases almost to zero (particles got stuck!).

![Figure 4.32: Typical course of mean square displacement of a) propane and b) propylene in the ionic liquid $[\text{BMIM}]^+ [\text{BTA}]^-$ vs. molecular dynamics simulation time. The decrease in MSD after the time-step 60 and no change of MSD after time-step 160 can be attributed to the „freeze effect“: the molecules of interest fluctuate within the limited volume and do not move further from the initial position.](image)

6. Calculating diffusion coefficients: The mean squared displacement of atoms in a simulation is computed by its definition

$$MSD = \langle [r_i(t) - r_i(0)]^2 \rangle$$

where $r_i$ denotes the position vector of the residue (molecule/molecular group/atom), and the angular brackets denote averaging over all choices of time origin within a dynamics trajectory.

\textsuperscript{24}In parallel test calculations, GROMACS MD simulation program [167] was used. The GROMACS trajectories can be read in with the visualisation program VMD (Visual Molecular Dynamics) [261] or gOpenmol [262, 263], where further analysis is possible.
To check whether the calculation of the mean squared displacement has been successful, the logarithm of the MSD value can be plotted against the logarithm of the appropriate timestep and, if the calculation has converged, a more or less straight line is obtained. If the line is fluctuating, the production run of the calculation must be repeated.

The mean squared displacement contains information on the diffusivity. In a liquid system, mean squared displacement ideally increases linearly with time.

The (self) diffusion coefficient of a molecular species (MS), undergoing random Brownian motion in three dimensions is evaluated from the limiting slope of the line of best fit (linear regression, \( y = ax + b \)) of the mean square displacement as a function of time, that is:

\[
D_{\text{MS}} = \frac{1}{6N_{\text{MS}}} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N_{\text{MS}}} \langle [r_i(t) - r_i(0)]^2 \rangle
\]

where \( N \) is the number of diffusive species in the system and \( \frac{d}{dt}[r_i(t) - r_i(0)]^2 \) is the slope of the line the diagram, \( a \). Therefore, this simplifies to (for the correct derivation with explanation see [115]):

\[
D_{\text{MS}} = \frac{a}{6}
\]

It should be noted that when constructing the linear line of the best fit into the graph, it is crucial to discard the first 10 - 20% of the simulation time since further equilibration may still have taken place. Therefore, parameter \( b \) is usually not zero. Also, a recommendation of experienced researchers is to remove the last 40 - 50% of the simulation or, if necessary, even more. Fig. 4.33 illustrates the decision making for the simulation values that should be included in the evaluation. The lines of best fit, which are needed for obtaining the slope \( a \) of the graph are also included.

The next section presents the results from the performed molecular dynamics computations.

7. Results form MD case study: Diffusion coefficients of propylene and propane in the chosen ionic liquid have been calculated at 298.15 K. As there are four molecules of propylene in one system and four molecules of propane in the other, the number \( N \) of diffusing atoms to be specified in the above equation is 36 for propylene, and 44 for propane respectively. Table 4.17 shows the computed results for propylene and propane at 298.15 K.

There is no experimental data available on diffusion coefficients in ionic liquids yet. In order to get an idea of the accuracy of molecular dynamics simulations, another computation has been performed on a well-understood system, the diffusion of oxygen in water. As indicated in table 4.18, a significant deviation is determined when computed and experimental data is compared.

A few simulations performed here with slightly different initial conditions could not be reproduced with respect to diffusion coefficients, which confirms the generally known fact
4.4. PROCESS PARAMETERS FROM MOLECULAR MODELLING

Figure 4.33: Evaluation of appropriate selection for „Mean Squared Displacement“ vs. timestep. a) What line to take in case of propylene? (Resubmit the calculation!) b) Straightforward solution for both propylene and propane.

Table 4.17: Computed diffusion coefficients in the ionic liquid at 298,15 K

<table>
<thead>
<tr>
<th>system</th>
<th>Diffusivity (298,15 K) [m²s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene - Ionic Liquid</td>
<td>2,83·10⁻⁸</td>
</tr>
<tr>
<td>Propane - Ionic Liquid</td>
<td>1,83·10⁻⁸</td>
</tr>
</tbody>
</table>

Table 4.18: Diffusion coefficients of oxygen in water at 298,15 K

<table>
<thead>
<tr>
<th>Diffusivity (298,15 K) [m²s⁻¹]</th>
<th>Computed</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen - Water</td>
<td>2,16·10⁻⁸</td>
<td>2,51·10⁻⁹</td>
</tr>
</tbody>
</table>
considering MD simulations. Many different runs with different initial geometries are needed for thorough evaluation of system’s behaviour, where many of these runs must be discarded\textsuperscript{25}. Sources of errors in MD simulations are various. The minimization, relaxation as well as the production run are all based on molecular mechanics. As mentioned in introductory section, the correct and approved force field is a crucial prerequisite to obtain accurate results. Due to the limited selection to choose from and the wide range of elements involved, it is assumed that the force field contributes to the error to a large degree.

Moreover, the defined number of molecules of the system is too small to obtain good accuracy, which increases with the number of molecules. Calculating non-bonded interactions only to a certain distance imparts an error in the calculation. If the cut-off radius is fairly large, this error will be very minimal due to the small amount of interaction at long distances [155]. This is why many bulk-liquid simulations usually incorporate 1000 molecules or more (only around 90 molecules have been used in this work). As the cut-off radius is decreased, the associated error increases.

Another issue contributing to the non-reproducibility is the number of dynamics steps. Since molecular dynamics is a statistical process, an increase in dynamics steps raises the accuracy of the simulation.

The margin for extending the system to be analyzed is also limited in this work. To obtain reasonable simulation results, the cell should contain 1000 molecules or more. A lack of CPU power (demo version of \textit{Materials Studio} could only be run on single personal computers and could not be parallelized for usage at the computer center), however, put decisive limitations on the computation of diffusion coefficients in this work. Furthermore, force fields must be developed, which can be more easily parameterised for completely new systems. Otherwise, the MD as a technique can not enter the serious engineering practice.

4.5 Conclusions

Based on the theoretical considerations gained in this chapter, I wish to recapitulate the findings referring to the desired properties for a potential carrier, which can be used in the (solid or liquid) carrier membranes.

Firstly, it is desired that the permeant-carrier reaction does show a very small (\(<5\,\text{kJ/mol}\)) or preferably do not show any activation barrier, i.e. any evident transition state or energy maximum along the reaction path coordinate. The process is rather to be seen as an adsorption, or what is classically considered to be physisorption, than as a (chemical) absorption. Its kinetics is thereby limited only by the diffusion transport in the membrane.

\textsuperscript{25}According to the support of the software producer Accelrys, deviations of one order of magnitude are likely to be obtained. Generally it can be stated that diffusion coefficients in polymers and liquids calculated with MD methods lie within 2 orders of magnitude below or above the measured values. However, they give very good account for the relative behavior of transported species. In this way these method have some predictive character. For instance one can evaluate water transport in two different polymers and draw the conclusion that one polymer is more permeable than the other. However, no absolute permeabilities can be obtained.
matrix material and not by the intrinsic reaction kinetics.

Secondly, the calculated reaction enthalpies for the permeant-carrier reaction using DFT methods (BP, BLYP or B3LYP) must lie preferably between -200 and -100 kJ/mol. This range is based on electronic energies without thermal corrections.

The calculated values thereby - independently of the software used - usually exceed the experimental values. Compounds, where the calculated enthalpy is above -40 kJ/mol may not be of any advantage. However, closer evaluation is still needed, dependant on the particular method and software used.

Another heuristic rule of the thumb may be added to those stated in chapter 2: the addition of the desired permeant to the carrier compound should preferably be of coordination nature. In addition reaction no covalent bond should be formed. The higher reaction enthalpies for the coordinating addition reactions are of advantage, since the control over the (reverse) reaction is easier and more economical to achieve at higher temperatures than at temperatures below ambient. The ligand plays a crucial role in the coordination of the metal providing suitable active site environment and influencing solubility. Ligand should also prevent the metal leaching. For oxygen 5-site and for olefins 3-site coordinating ligands should be developed.

Finally, let me shortly evaluate the tools used in this chapter. Several quantum chemistry programs were used and compared. None of them could precisely reproduce the experimental data. Therefore, today, quantum mechanics can be used only for qualitative understanding of the molecular mechanisms and to certain extent for prediction of chemistry behaviour of unknown compounds.

Due to the inaccuracy and extensive computing time, molecular dynamics for calculation of diffusion coefficients in case of complex systems is still inferior to group contribution methods. However, it enables the qualitative comparison of diffusion coefficients of different compounds in the liquid relative to each other.

Having in mind an industrial engineer, who is permanently standing under heavy deadline pressure due to economical realities, he or she might not have the time to choose from abundance of software, evaluate outputs of several calculations on „different levels of theory“ and spend hours to interpret them, nor would he or she dare to rely on their results. A universal workable solution in the field of quantum mechanics methods is still required. Until then, simulation will be the domain of academic world and experimental work - as described in the next chapter - can not be avoided and remains a merit.
5 Materials and Experimental

In this chapter, experimental work performed on the materials used in this thesis and on the self-made liquid membranes composed of these materials is presented.

Firstly, the necessary theoretical background to the novel materials that are used as components for the liquid membranes will be given. In particular, relevant properties of different ionic liquids along with the respective investigation methods are focused. Next, various types of (in)organic porous supports and their combination with ionic liquids, i.e. the preparation of liquid membranes is reported. Some carriers are also considered in this context. Finally, the produced liquid membranes are characterised in terms of flux and selectivity.

5.1 Ionic Liquids

Ionic liquids (ILs) are organic salts with melting points below ambient temperature [264]. In general, an ionic liquid is a liquid that consists only of ions, i.e. no extra solvent is present. This means actually that ionic liquid is an ionic melt. Liquidity at low temperatures, mostly below 100 °C, can in almost all cases be attributed to the flexible form of the respective cation, which furthermore displays low molecular symmetry. For example, bulky imidazolium and pyridinium cation derivatives prevent regular ordering of molecules within the liquid, yielding amorphous solids when cooled down to very low temperatures with e.g. liquid nitrogen during differential scanning calorimetry (DSC) procedures. Small, electronically „hard” anions like Cl\(^-\) or NO\(_3\)\(^-\) are rarely encountered in ILs. However, compounds having these anions are often used as the precursor materials for the synthesis of the „real” ILs. Instead of such hard ions, anions displaying strong electron-delocalisation like BTA (bis-(trifluoromethylsulfonyl)amide) are employed, which significantly lower the viscosity. A variety of potential cations and anions that can be combined to ionic liquids is shown in Fig. 5.1.

It has to be noted here that some ionic liquids do crystallise in ordered structures. For instance, spontaneous solidification to a crystalline form of IL 1-methyl-3-methylimidazolium methyl sulfate (Fig. 5.2, compound g)) at room temperature was observed. The effect is not well understood, but implies that ILs might be considered to be thermodynamically unstable, i.e. that they are metastable undercooled compounds.

Not all combinations of ions will automatically lead to the liquid or low melting point IL. Nor will such IL automatically have desired properties. There are still no worked-out recipes available, which would replace intuition in the synthesis of ionic liquids. Nevertheless, cations and anions of ionic liquids can be independently modified and thus provide,
in terms of combinatorial chemistry, a great potential for the polarity, viscosity, surface tension and other properties to be appropriately customised for specific tasks. In particular, the chemical behaviour can be altered by changing the length and the functionality of the side groups attached to the parent compound.

5.1.1 How Special are Ionic Liquids?

The unique property, common to all ionic liquids is the lack of measurable vapour pressure. (Recent publications state values of $10^{-11}$ Pa.) This property has opened new research areas. ILs have been particularly investigated as alternative solvents for transition metal catalysis [265, 266]. In the biphasic systems (organic solvent/IL) they enable easier product isolation and recovery of homogeneous catalysts [267]. The same holds for their use in different distillation applications [268]. Ionic liquids are also excellent extraction media for transition metals [269], good solvents for many different catalysts [270, 271] and they display different absorption/desorption properties for different gases and vapours. Therefore they could also be used as entrainers in extractive distillation. Meanwhile, the application field of ILs has been extended to heat transfer, lubrication and hydraulic media, to electrochemical applications [272, 273], etc. An increased interest has also been shown in theoretical understanding of the behavior of ILs on molecular level [274].

Moreover, the lack of vapour pressure made ionic liquids - in addition to other physical properties stated above - the ideal materials for the active phase in liquid membranes, especially for gas and vapour separations. Particularly designed ILs have become commercially available, but are still costly in comparison to classical solvents. However, extremely small amounts of valuable membrane phase are actually necessary to generate a supported liquid membrane. This encouraged me to test these unique liquids. In spite of their high costs, they might posses the potential for being economically used in large scale membrane gas and vapour separation processes.
5.1.2 Ionic Liquids Used in the Thesis

Several ionic liquids were made available by Prof. Wasserscheid or were produced in my own synthetical attempts. Some of them are shown in Fig. 5.2. However, in this thesis it was not aimed at their systematical or full characterisation. I rather focused on some properties, substantial for membrane applications.

Figure 5.2: Structures of more common ionic liquids used in the experiments

Since limited amount of materials appeared to be the most prohibitive for conducting of several experiments, I restricted my choice to those compounds, where at least 30-50 g were available.
5.1.3 Properties of Neat Ionic Liquids

5.1.4 Viscosity and density

For a solvent to be successfully used for engineering purposes, low viscosity is of great importance since it crucially determines mass and heat transport behaviour. Dynamic (or absolute) viscosity $\eta$ is connected with kinematic viscosity $\nu$ through the density of the liquid:

$$\nu = \frac{\eta}{\rho}.$$

Density of ionic liquids usually lies between 1000 and 1500 kg/m$^3$ (For example, density measurements at 20°C of compounds c), d), e), h), i), j), k), l), m) and n) in Fig. 5.2, gave following values: 1,173, 1,296, 1,295, 1,265, 1,242, 1,202, 1,53, 1,309, 1,25 and 1,46 g/ml, respectively.). In comparison with the conventional organic solvents, ionic liquids have relatively high viscosity and recent endeavours are directed towards synthesis of ILs with low viscosities [275]. Viscosity is highly temperature dependant, therefore a fair comparison with related inorganic molten salts with melting points above 350°C, where ILs readily decompose, is not possible. In Fig. 5.3 the results of measurement of viscosity of two ionic liquids is presented. The viscosity of these two example systems is important because they are needed for determination of diffusion coefficients in the published estimation equations (cf. Chapter 3).

Figure 5.3: Viscosity of two ionic liquids: a) $[\text{BMIM}]^+ [\text{BTA}]^-$, measured with two methods b) $[\text{BMIM}]^+ [\text{CuCl}_2]^-$.

It was found that except at extremely low shear rates $[\text{BMIM}]^+ [\text{BTA}]^-$ (Fig. 5.2, compound a), $\rho=1450$ kg/m$^3$) as well as $[\text{BMIM}]^+ [\text{CuCl}_2]^-$ (Fig. 5.2, compound o)) behave strictly as Newtonian liquids within the temperature window from 20 to 120°C, i.e. the viscosity is not a function of the shear rate applied.

The viscosity of another ionic liquid, namely $[\text{NEt}_2\text{-BMIM}]^+ [\text{BTA}]^-$ (Fig. 5.2, compound b), density $\rho=1570$ kg/m$^3$) was also measured. The IL is 30 times more viscous at room
temperature than \([\text{BMIM}]^+ [\text{BTA}]^-\). One can see in this example that the modification of ionic liquid, here by adding a functional group to the side chain of the cation, changes the viscosity significantly.

### 5.1.5 Relative permittivity

Relative permittivity \(\varepsilon_r\) is the quantity that describes the extent of polarisation of the considered compound when it is put into an external electrical field. In chemistry, relative permittivity also characterises the solvation properties of a given medium because the solvent itself generates an electrical field on the molecular scale that can be compared to the one generated by a condenser. The polarisation effects in question are caused due to the dipole and higher molecular moments. Since quantum chemical calculations by application of continuous solvation models require experimentally acquired relative permittivity \(\varepsilon_r\) for description of the solutes environment, I have tried to obtain some values for ionic liquids.

In the gas phase, ionic liquids (i.e. theoretical construct of one cation and one anion) display distinctive dipole moments as do isolated ions, too. In an ensemble, i.e. in the condensed liquid phase, this might no be case, although certain orientational effects contributing to the overall net-dipole are very likely to occur - we do not know enough at present about these structural facts in ILs.

Choosing the measurement method proved to be difficult: ionic liquids are electrolytes that conduct electrical current, therefore classical measurements of their relative permittivities through the change of the condenser capacity within LC-oscillator - where the measurements of dipole moments depend on frequency - is not possible [276]. Insulated condenser electrodes that made the measurement possible (no short-cut) lead to the signal-to-noise ratio near 1, which makes the method useless. The work-around method is the determination of propagation velocity of electromagnetic wave\(^1\) in the respective medium. However, one can not obtain the values directly from the theoretical principles and one must calibrate the apparatus with known substances as this is presented in Fig. 5.4.

Relative permittivity constants for several ionic liquids are given in Table 5.1. The results were obtained by several reproducible measurements. Additionally, results from measurements of refraction index \(n\) at 20°C against air are also included.

The measured values are in good agreement with published results of related ionic liquids [254]. Another route to the relative permittivity constants can be, at least theoretically, approached by measurement of refraction index \(n\). It is given through the relationship:

\[
n = \frac{c}{v},
\]

where \(c\) is the speed of light in vacuum (or air) and \(v\) is the speed of light in the respective medium. For common materials, refraction index is greater 1, recently however, so called metamaterials with negative values were discovered [278].

\(^1\)The apparatus [277] was kindly provided by Mr. M. Zadow, Zadow Electronics, Cremlingen, Germany.
propagation of electromagnetic waves are:

\[ c^2 = \frac{1}{\mu_0 \epsilon_0} \]
\[ v^2 = \frac{1}{\mu_0 \mu_r \epsilon_0 \epsilon_r} \]

where \( \mu_0 \) and \( \epsilon_0 \) are fundamental nature constants, magnetic permeability and permittivity of vacuum. \( \mu_r \) and \( \epsilon_r \) are relative magnetic permeability and the relative permittivity. Dividing both equations yields:

\[ \frac{c^2}{v^2} = \frac{\mu_0 \mu_r \epsilon_0 \epsilon_r}{\mu_0 \epsilon_0 \epsilon_r} = \frac{\mu_0 \mu_r \epsilon_0 \epsilon_r}{\mu_0 \epsilon_0 \epsilon_r} \]
\[ n = \sqrt{\mu_r \epsilon_r} \quad \text{(Maxwell relation)} \]

For diamagnetic substances like water or ionic liquids, where all electrons are paired in closed shells, relative magnetic permeability is close to 1, therefore theoretically an approximation:

\[ n \approx \sqrt{\epsilon_r} \]

\[ \text{can be used. Unfortunately, this Maxwell relation is not accurate enough for practical purposes. For example, the index of refraction for water is 1.332, its relative permittivity is reported to be between 79-81. The speed of light changes in any medium due to electromagnetic interaction with the molecules. The equation above does not account for} \]

Figure 5.4: Measurement of permittivity: a) apparatus b) calibration curve (air 1.0; cyclohexane 2.023; dichloromethane 8.93; acetone 20.7; ethanol 24.55; acetonitrile 36.64; DMSO 46.7; water 81; formamide 110)
### Table 5.1: Measured relative permittivity constants and index of refraction of different ionic liquids (the structures of ILs RWQ and IP-PW(C) are confidential)

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Compound</th>
<th>Signal $y$</th>
<th>$\epsilon_r$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM]$^+$ [BTA]$^-$</td>
<td>a)</td>
<td>1,494</td>
<td>18.1</td>
<td>1,4269</td>
</tr>
<tr>
<td>[EMIM]$^+$ [EtSO$_4$$^-$$]$</td>
<td>i)</td>
<td>1,799</td>
<td>93.9</td>
<td>1,4640</td>
</tr>
<tr>
<td>[EtPy]$^+$ [EtSO$_4$$^-$$]$</td>
<td>m)</td>
<td>1,615</td>
<td>34.8</td>
<td>1,4973</td>
</tr>
<tr>
<td>[NEt$_2$-BMIM]$^+$ [BTA]$^-$$</td>
<td>$</td>
<td>b)</td>
<td>1,356</td>
<td>8.6</td>
</tr>
<tr>
<td>[BMMIM]$^+$ [BTA]$^-$$</td>
<td>$</td>
<td>d)</td>
<td>1,427</td>
<td>12.6</td>
</tr>
<tr>
<td>[4-MOPy]$^+$ [BTA]$^-$$</td>
<td>$</td>
<td>l)</td>
<td>1,357</td>
<td>8.6</td>
</tr>
<tr>
<td>[HMIM]$^+$ [PF$_6$$^-$$]$</td>
<td>d)</td>
<td>1,341</td>
<td>8.0</td>
<td>1,4169</td>
</tr>
<tr>
<td>[RWQ]</td>
<td>conf.</td>
<td>1,319</td>
<td>7.0</td>
<td>1,4715</td>
</tr>
<tr>
<td>[IP-PW(C)]</td>
<td>conf.</td>
<td>1,476</td>
<td>16.5</td>
<td>1,4888</td>
</tr>
<tr>
<td>[MMIM]$^+$ [MeSO$_4$$^-$$]$</td>
<td>g)</td>
<td>1,582</td>
<td>29.2</td>
<td>1,4852</td>
</tr>
</tbody>
</table>

Light absorption, which has to be measured separately and is beyond the scope of this work.$^2$

### 5.1.6 Solubility of Gases and Vapours in Neat ILs

As mentioned in the introduction, the solution-diffusion model is the classical view of the mass transport through dense membranes. The applicability of a given ionic liquid for a separation of particular gas or vapour from a mixture by a liquid membrane can be primarily estimated by gas absorption/desorption measurements. Both kinetics and thermodynamics play a crucial role: the equilibria must be achieved fast and the liquid must be easily discharged. Since the diffusion coefficients of species with similar molecular mass have similar values - often very close within the same order of magnitude - logically consistent they have an underlying importance compared to solubilities. Therefore, gas/vapour solubility will be looked at closely first.

### Preliminary Screening Experiments

Preliminary informative experiments are conducted in a simple laboratory experimental setup (Fig. 5.5a, b) also used for educational purposes [280]. The advantage of this apparatus, which was primarily built for measuring of CO$_2$ absorption in water, is that small storage tank (ST) is easily filled with different gases and vapours in succession. The problem is the proportionally high volume (750 ml) of the gas/vapour volume compared to approximately 50 ml of the liquid volume that can be put into the reaction vessel (R, Fig. 5.5c). Therefore, the measurement of pressure decrease during the absorption leads to inaccuracies, especially in case of very low liquid absorption capacities.$^2$

---

$^2$For substances that absorb and refract light, a complex index of refraction must be worked with, which is beyond the scope of this thesis. For theoretical background refer to e.g. [279]
5. MATERIALS AND EXPERIMENTAL

Figure 5.5: Gas solubility measurements: a) scheme of experimental setup b) photograph of the apparatus c) reaction vessel with IL

Experiments are conducted in several steps in the following order: the reactor is filled with ionic liquid and evacuated under stirring using vacuum line and valve V3. Then, the dosing coil is filled with gas or vapour using valves V1 and V2. Valve V2 is then opened and pressure decrease is monitored with time.

In two subsequent experimental sequences, two ionic liquids ([BMIM]⁺ [BTA]⁻ and [NEt₂-BMIM]⁺ [BTA]⁻) are examined. Some results of absorption of different gases are shown in Fig. 5.6a. In all cases, application of vacuum after absorption causes very strong effervescence, pictured in Fig. 5.6b.

Figure 5.6: Qualitative exploration of gas and vapour solubilities in ionic liquids: a) time dependent absorption (full symbols: [BMIM]⁺ [BTA]⁻; empty symbols and (A): [NEt₂-BMIM]⁺ [BTA]⁻) b) effervescence during desorption

Preliminary observations can be summarised:
Due to the higher viscosity of functionalised ionic liquid \([	ext{NEt}_2\text{-BMIM}]^+ [\text{BTA}]^-\), the absorption time needed for reaching gas-liquid equilibrium approximately doubles. The absolute solubility differs strongly for different compounds from IL to IL, but generally shows the same relative trends for the same gases and vapors.

The absorption of permanent gases nitrogen, oxygen and hydrogen is extremely low. Because of the poor pressure resolution of the pressure transducer and inappropriately big volume of the measuring system, the differences in absorption behavior cannot be revealed.

Both ionic liquids darken slightly in their appearance when they are contacted with \(\text{SO}_2\), where the strongest absorption occurs. Even after long evacuation they retain pungent odour. Pure ionic liquids have no vapour pressure, therefore they can not and do usually not smell. Thus, it can be concluded that desorption process is either not reversible or some kind of partial reaction takes place. Surprisingly, no further changes of both liquids (e.g. in viscosity or appearance) could be noticed even after a continuous exposure to \(\text{SO}_2\) over a few months.

In contrast, \(\text{H}_2\text{S}\) could be tracelessly removed from the liquids. However, the lack of special room for handling this poisonous gas, as well as in case of \(\text{SO}_2\), turned out to be prohibitive for all further experiments.

Experiments with organic vapours methane, ethane and ethylene show comparable solubility of ethane and ethylene and lower solubility of methane. Preparation of silver nitrate saturated ionic liquid (via ultra sound method) do not lead to an enhancement of the absorption capacity for ethylene. The solubility of silver nitrate turned out to be less than 0,1 %. At the end of the experiments with silver nitrate, ionic liquids contain black precipitate of elemental silver.

Yet another test was performed with \(\text{NH}_3\), where the absorption capacity is comparable to that of \(\text{SO}_2\). Almost no effervescence could be observed during desorption. Nucleophilic attack of ammonia lone electron pair to imidazolium residues may take place here, leading to alkyl-exchange reaction (transalkylation). When contacted to ammonia, the ionic liquid \([\text{BMIM}]^+ [\text{BTA}]^-\) becomes visibly less viscous, this effect being irreversible (probably due to the chemical decomposition).

For detailed study of chemical interactions of the more reactive gases \(\text{SO}_2\), \(\text{H}_2\text{S}\) and \(\text{NH}_3\) an investigation of samples with NMR would be necessary, which was, however, not available.

**Experiments with chosen systems**

In a refined experimental setup (Fig. 5.7), the volume ratio gas to liquid is reduced. Apart from increasing the measurement accuracy due to the smaller gas phase volume of the absorption cell, the main advantage of this setup is the possibility to more precisely control the amount of gas in the gas vessel \(V_G\). Furthermore, it enables controlled desorption of gas or vapour phase out from the reaction vessel \(V_A\), where pressures up to 6 bar can
be measured\textsuperscript{3}. Gas-liquid equilibria measurements, expressed in term of modified Henry law can be conducted at different starting and intermediate pressures. Some 20 to 40 g (or corresponding volume) of ionic liquid ($V_L$) is put into the stirred chamber $V_A$. IL is evacuated at $p < 10^{-4}$ bar for about 15 min for each experiment. The procedure is started by pressurising a certain amount of gas or vapour into the chamber $V_G$. The valve V1 is opened shortly for pressure equalisation and then closed. Pressure decrease in compartment $V_A$ is measured as a function of time, although only the equilibrium values are of interest. After equilibrium is reached, the gas vessel $V_G$ is evacuated. Valve V1 is opened again shortly giving new starting gas phase pressure at loaded liquid. Form now on, desorption of the gas or vapour from the liquid takes place in the vessel $V_A$. In this manner, per single charging of the liquid two values are obtained: one value comes from the absorption and the other from desorption. Approaching equilibrium from different initial conditions compensates the error of each run, which is caused by not waiting long enough for reaching final equilibrium.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{absorption-desorption_apparatus.png}
\caption{Absorption-desorption apparatus: a) scheme; photographs of b) the apparatus and c) reaction vessel}
\end{figure}

\textit{Carbon dioxide, methane, hydrogen, nitrogen}: The primary purpose of this investigation was to show that it is, in principle, possible to separate carbon dioxide from a mixture made of gases typically found in natural gas.

The absorption-desorption experiments were repeated at different starting pressures (400, 700, 1200, 1700 and 2800 mbar). The pressure difference between the initial and final equilibrium state during the absorption and desorption, respectively, yielded amount of gas in mol transported between the gas/vapour and the liquid phase (simple integral mass/mol balance). Hereby, being far from condensation point of the respective gases and vapours, ideal gas law could be used. Knowing the mass and density of the pure liquid, which were assumed to remain unchanged during the experiments, Henry coefficients were obtained by correlating the amount of gas/vapour in the liquid with corresponding vapour pressure.

\textsuperscript{3}Pressures up to 6 bar are realistic to be applied on liquid membranes, therefore I have taken this pressure range as relevant.
Absorption kinetic parameters $k_{\text{eff}}$, which only hold for the experimental setup used, were calculated applying the equation

$$J(t') = -\frac{dn_{\text{transported}}(t)}{dt} = -k_{\text{eff},i} \cdot dc(t) = -k_{\text{eff},i} \left( \frac{p_{\text{gas}}(t)}{H} - c_{\text{liquid}}(t) \right)$$

by solving it with forward integration iteratively through fitting the curve to the experimental absorption data (Fig. 5.8).

Figure 5.8: Absorption of N$_2$, H$_2$, CO$_2$ and CH$_4$ in [BMIM]$^+\ [\text{BTA}]^-$: a) rates of absorption as determined by simple iterative process (only one measurement at 1700 mbar starting pressure is shown) b) gas-liquid equilibria expressed in terms of Henry coefficients

One can see that all gases are absorbed into the liquid with the comparable transfer rates. The transport of hydrogen is slightly faster than that of other three gases. CO$_2$ absorbs ten times better in the ionic liquid than CH$_4$. Nitrogen and hydrogen are not very soluble in the chosen ionic liquid and hydrogen is less soluble than nitrogen. This is not surprising, since for the solubility the area to volume ratio of the molecule is decisive for its solubility (cf. 4.3.7). The results for diethylamino functionalised IL, [NEt$_2$-BMIM]$^+\ [\text{BTA}]^-$, not explicitly shown here, displayed lower solubility for carbon dioxide and slower absorption rate, the latter being caused by higher viscosity. This confirmed the trend already observed in preliminary study. This ionic liquid was not used in any further experiments.

**Oxygen, nitrogen:** For solubilities of oxygen and nitrogen, four ionic liquids were tested at two different temperatures, namely 25°C and 80°C. The results are presented in Fig. 5.9 The best solubility of oxygen is given in [BMIM]$^+\ [\text{BTA}]^-$. Because of this fact and because of the available amounts, further studies were made only with [BMIM]$^+\ [\text{BTA}]^-$. The selectivity of the produced membranes will however be dependant on the ratio of solubilities which is the best in N-ethyl-pyridinium-ethylsulfate at 80°C. The ratios however, are all below the factor of two, which can be compared to solubility ratios in other

---

4The amine functional group attached to butyl residue of imidazolium cation might need some protic environment in order to reactively interact with acid gases like CO$_2$. It seems that the lone electron pair of the amine group is well coordinated and can not be set free within IL. Accordingly, CO$_2$ is merely physically dissolved in IL.
5. MATERIALS AND EXPERIMENTAL

Figure 5.9: Absorption of $N_2$ and $O_2$ in terms of Henry coefficients (given as slopes of the lines in unit mbar m$^3$/mol) in ILs a) [BMIM]$^+$ [BTA]$^-$ b) [EtPy]$^+$ [BTA]$^-$ c) [EtPy]$^+$ [EtSO4]$^-$ d) [2-M$_3$ABuOH]$^+$ [BTA]$^-$ (these compounds correspond to a), k), m) and n) in Fig. 5.2, respectively.

solvents [256]. Furthermore, the solubilities of both nitrogen and oxygen are extremely low and at higher temperatures typically a decrease in gas solubility is observed, as this is also known from other gas-liquid systems.

Propane, propylene, butane and 1-butene Since propane/propylene separation is today one of the most important separations worldwide, I have decided to include this problem in the experimental part of my thesis. I performed some experiments on solubility of this feedstock in [BMIM]$^+$ [BTA]$^-$, all the measurements in this liquid being conducted at ambient temperature. The results are shown in Fig. 5.10a. Additionally, some measurements for butane and 1-butene solubility are also included.

Whereas for C3 compounds one still obtains a straight line in the diagram, which does go through the diagram origin, this is not the case for C4 compounds. The vapour pressure of C4 compounds is so near the condensation point at room temperature and pressures of 2 bar, that it is no longer allowed to use the ideal solubility approximation according to Henry. (Negative values for the intercept of the fitted straight line suggest that the condensation in the presence of ionic liquid is likely to occur.)

From the theoretical reasoning from the previous chapter, I wanted to confirm that propylene does not coordinate or react with the [CuCl$_2$]$^-$ anion of corresponding ionic liquid.
5.1. IONIC LIQUIDS

Figure 5.10: Absorption in \([\text{BMIM}]^+ [\text{BTA}]^-\) of a) propylene and propane b) 1-butene and butane (Henry coefficients are given as slopes of the lines in unit mbar m$^3$/mol)

\([\text{BMIM}]^+ [\text{CuCl}_2]^-.\) The absorption data were measured at different temperatures in order to overcome the activation barrier and to see the influence of the temperature on equilibrium, if we should have any reaction. However, for the purpose of fast screening, only one pressure-concentration point was measured. It is here for the first time that I express the Henry coefficient in its „real“ (pressure) units. In contrast to the measurements above, here I also measure the concentration as mol fraction $x_i$ that is not dependant on temperature dependant density. The results for propane and propylene are presented in Fig. 5.11.

Figure 5.11: Absorption of propylene and propane in \([\text{BMIM}]^+ [\text{CuCl}_2]^-\) (only one point was taken per measurement, Henry coefficient is given in SI unit Pa)

As above, one can clearly see that the solubility decreases with increasing temperature. There occurs no reaction, otherwise the ratios of liquid phase concentrations would be much larger than factor $3^5$, which is due to the physical solubility only. We [281] encoun-

\(^5\)The total amount of ionic liquid was about 30 g (0,1 mol) in each experiment, whereas the amount of vapor phase at applied pressures was about 0.0023 mol. In a reaction therefore, almost all of propylene could disappear.
tered problems with reproducible propane solubility measurements, therefore not all but only reliable data are presented in Tab. 5.2.

Table 5.2: Measured Henry coefficients from Fig. 5.11

<table>
<thead>
<tr>
<th>$T$ [°C]</th>
<th>$H_{\text{en,exp}}$ [Pa]</th>
<th>$H_{\text{an,exp}}$ [Pa]</th>
<th>$\frac{H_{\text{en}}}{H_{\text{an}}}$ exp. ratio</th>
<th>$H_{\text{en,calc}}$ [Pa]</th>
<th>$H_{\text{an,calc}}$ [Pa]</th>
<th>$\frac{H_{\text{en}}}{H_{\text{an}}}$ calc. ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0,736·10^{-7}</td>
<td>2,829·10^{-7}</td>
<td>3,056 (intr.)</td>
<td>0,842·10^{-7}</td>
<td>3,827·10^{-7}</td>
<td>4,544</td>
</tr>
<tr>
<td>30</td>
<td>1,116·10^{-7}</td>
<td>5,056·10^{-7}</td>
<td></td>
<td>1,085·10^{-7}</td>
<td>4,671·10^{-7}</td>
<td>4,306</td>
</tr>
<tr>
<td>35</td>
<td>1,326·10^{-7}</td>
<td>5,056·10^{-7}</td>
<td></td>
<td>1,648·10^{-7}</td>
<td>6,422·10^{-7}</td>
<td>3,897</td>
</tr>
<tr>
<td>50</td>
<td>1,373·10^{-7}</td>
<td>5,056·10^{-7}</td>
<td></td>
<td>1,959·10^{-7}</td>
<td>7,288·10^{-7}</td>
<td>3,721</td>
</tr>
<tr>
<td>60</td>
<td>1,763·10^{-7}</td>
<td>5,056·10^{-7}</td>
<td></td>
<td>2,615·10^{-7}</td>
<td>8,923·10^{-7}</td>
<td>3,412</td>
</tr>
<tr>
<td>80</td>
<td>1,763·10^{-7}</td>
<td>5,056·10^{-7}</td>
<td></td>
<td>2,615·10^{-7}</td>
<td>8,923·10^{-7}</td>
<td>3,412</td>
</tr>
</tbody>
</table>

We can now compare the measured Henry coefficients with the values from COSMOtherm calculation from the previous chapter. Since the diagram presented there does not provide enough details, tabulated values for propane and propylene are also provided. For propylene, calculated data are in good agreement with experimental values, but give a stronger temperature dependance. For propane, the calculated solubility is far too low (high Henry coefficient means low solubility). However, one has to have in mind, that these values are based only on theoretical considerations and vapour pressure that can be included in COSMOtherm calculation is not explicitly given by e.g. Antoine or Wagner equation (this is reasonable, since this equations only hold in certain „undercritical” conditions, where two phase system still exists). Therefore, trends can be well predicted, for instance, in both cases we observe that the ratio of solubilities decreases with increasing temperature. For membrane separations, this means to conduct the separation at low temperatures in order to increase selectivity.

5.2 Inorganic Supports

So far, I have described some ionic liquids and their properties. In order to assemble supported liquid membranes, one also requires appropriate porous supports. When contacted with solvents in general, organic membranes show strong swelling behavior. The main advantage of inorganic materials that membranes are composed of is, in contrast, their stability because of the complete lacking of the swelling phenomenon. Therefore, with the exception of one type of PTFE membranes\(^6\), which I will not refer to, I have decided to use only inorganic support materials for immobilising the ionic liquids. Some of the used supports that are either available on the market or were provided by different research institutions will be shortly presented.

When we talk about porous supports, we actually talk about porous materials that are used as membranes themselves. Most of the research on supported liquid membranes so

\(^6\)The suggestion made by Prof. Caro, University of Hannover, was to use organic unpolar support in order guarantee the stabilisation of immobilized ionic liquids in the porous support. The proposed membranes were provided by Bohlender GmbH, Lauda, Germany.
5.2. INORGANIC SUPPORTS

far was conducted applying organic porous supports (e.g. Millipore membranes), therefore by taking inorganic membranes, we are entering the wholly new field.

5.2.1 Flat Supports

Pure Alumina Supports

A commercially available support „Anodisc” marketed by Whatman company possesses uniform thickness of only 60 µm, uniform pores of 200 nm in the support layer and on the top an active layer of 25 nm pore size with a thickness up to 2 µm (Fig. 5.12). The whole membrane is integrally build of the same material (Al₂O₃). These very brittle membranes of approx. 10 cm² area are currently used as one-way filters in microbiological research [282].

Figure 5.12: Whatman Al₂O₃ support: a) cross section b) diagonal cross section c) top view (25 nm active layer d) bottom cross section (200 nm) e) bottom view (200 nm)

In my own attempts to synthesise variations⁷ of such a support with larger areas, required for scale-up, I have found that the aluminium metal precursor must be of high purity (99.95%). The experimental setup is shown in Fig. 5.13a, whereas Fig. 5.13b and c show the problems if raw material is of low purity and its surface is not pretreated. In only one run, I was able to produce decent anodised films Fig. 5.13d.

Before anodising procedure, the surface must be pretreated and purified with 20% KOH. Low temperatures of about 4°C are crucial for successful anodisation process, i.e. for uniform dendritical growth of Al₂O₃. In the experiments, 3 M H₂SO₄ and 2 M H₃PO₄ were used as electrolytes. The applied anodisation voltage was 35 V. I was unfortunately not able to detach the anodised layer from the metal precursor with the available equipment. Some photographs of the obtained materials are shown in Fig. 5.14.

⁷Thinner supports would be of an advantage for enhancement of mass transport due to the shorter diffusion pathways in liquid membranes; on the other hand, thicker supports might be used in gas phase microreactor [283] in order to better control the residence time distribution.
Figure 5.13: Anodisation experiments: a) simple experimental setup without temperature control; b)-c) cathode and anode without pretreatment (deposited materials are $\text{Al}_2(\text{SO}_4)_3$ and $\text{Cu}_2\text{O}$); d) growth of $\text{Al}_2\text{O}_3$ on Al

Figure 5.14: Anodisation experiments: a) two adjacent $\text{Al}_2\text{O}_3$ layers and b) their detailed structure; c) the cleavage between the two layers containing the rest Al metal precursor; d) visualisation of Al rests in the produced material by amalgam method

I also developed the method for visualisation of presence of undesired aluminium metal rests in the anodised layer. Even if the product appears translucent, a short treatment with aqueous solution of mercury(II) acetate will produce amalgam forming crystal like growth within the anodised layer. It is important to notice that the pore sizes obtained are not distributed uniformly as in a commercial product. Here, more sophisticated technical development is necessary in order to obtain usable product [284, 285].

**Ceramic Supports on Woven Metal Fabric**

Creavis (Degussa) introduced interesting membrane products around year 2000. Actually, these products are nano- and ultrafiltration ceramic membranes with two available nominal pore sizes of 25 and 100 nm. These membranes are, although completely made of inorganic materials, quite flexible and can be bent within certain limits without being damaged. Like other ceramic membranes they are very polar and their main application area is water filtration. The woven metal is stainless steel. Newer membranes are based on glass fabrics.

Since the research work on this membranes was performed under contract, the essential results are treated confidentially.
5.2. INORGANIC SUPPORTS

Figure 5.15: Flexible inorganic membrane: a) sample membrane b) schematic composition c) surface with visible woven framework d)-e) details from the membrane surface

Metal Supports

Another interesting support, etched aluminium ultrafiltration membrane (Fig. 5.16), was kindly provided by GAP Handels AG.8

The pore size of this material lies between 0.5 and 8 µm. The inner of the pores is covered with mixed oxides. Therefore, support surface is not a metal and is hydrophilic. The transmembrane pressure stability by applying water reaches 20 bar.

8Contact: G. Oerkenyi, gap@swissworld.com, Switzerland
Silicon wafer supports (Fig. 5.17), provided by FluXXion can be manufactured by silicon (photo) etching as it is primarily used in electronic chip production.

in different pore size ranges (3.5 µm; 2.0 µm; 1.2 µm; 0.8 µm; 0.45 µm). The surface appears to be metallic. However it is covered with silicon nitride and is expected to be hydrophobic. The membranes are delivered with thin liquid protecting coating (glycerine) and must be degreased prior to the usage.

The membrane slits „holding” pores are very fragile due to the extreme thinness of the membrane of less then 1 µm. The thickness was estimated from SEM (Fig. 5.18) pictures to be only 800 nm and are therefore very attractive for the immobilisation of ionic liquids.

5.2.2 Tubular Supports

Standard Membrane Tubes

Tubular membranes, an example shown in Fig. 5.19a, are the most common commercial product in applications like micro-, ultra- or nanofiltration. Several companies supply these inorganic membranes. I have confined myself to use the products of only one pro-
5.2. INORGANIC SUPPORTS

Producer (HITK\textsuperscript{9}), whose products are known for a very few defects (pin-holes) in their active layer. The membranes are composed of several layers (Fig.5.19b, every one of them being oxide-based. Active layer made of Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} is designed in such a way that the mean pore size can be adjusted to 60 nm, 30 nm, 5 nm or even 0,9 nm. They are hydrophilic and can be made hydrophobic by the silylation process. However, this option was not used in the thesis.

![Figure 5.19: Tubular membrane by HITK: a) 10 cm long membrane b) cross-section displaying multilayered structure c) active layer](image)

Capillary Supports

Multilayered Ceramic Supports Multilayered ceramic capillary supports possess basically of the same macroscopic structure as do tubular supports. The difference lies only of the diameter of the supporting layer, (outer diameter is about 3 mm, inner diameter about 1 mm, Fig. 5.20a. The main advantage over the tubular supports is smaller membrane weight per m\textsuperscript{2} and higher packing density within the membrane module as this is is known in capillary organic membranes. Here too, I restricted myself to membranes produced by HITK, which also display the same mean pore diameters as stated above.

Extruded Supports Extruded inorganic capillary membranes are one among the latest developments in the field of inorganic membranes. Membranes used here were provided by the research institute IGB (Fraunhoferinstitut für Grenzflächen- und Bioverfahrenstechnik, Stuttgart) and the research department of Mann & Hummel (M&H) company. The extruded precursor displays integral symmetry, however final membrane is structured because of a delicate firing procedure. The details of the membrane are shown in Fig. 5.20b-d. The most common mean pore diameter is around 200 nm. Outer diameter is less than 2 mm, membrane thickness lies under 250 µm.

\textsuperscript{9}Hermsdorfer Institute for Technical Ceramics kindly provided their membranes, sometimes even tailor made, at our disposal.
5.3 Supported Liquid Membranes

So far, I have described raw materials, which liquid membranes are produced from. In this section, I will describe the preparation of liquid membranes therefrom and some tests and criteria for the evaluation of materials compatibility.

5.3.1 Preparation

Some of the above mentioned ionic liquids were immobilised in pure inorganic support by several methods. To mention the common ones only, the most simple among them is the complete immersion of the support into the chosen ionic liquid or its formulation. In this full impregnation case, one obtains membrane layers as thick as all porous support layers. One has to apply vacuum in order to remove the air or protective gas from the pores. In the second method one uses the fine brush, covering only one side of the membrane as this is presented in Fig. 5.21a. When Whatman membrane support is covered with ionic liquid it becomes translucent. This is not the case for other supports. In both preparation techniques surplus liquid is removed by carefully wiping both sides of the support with a soft paper tissue.

I could also produce fine aerosols of ionic liquids with a simple pump spray and in principle, spraying technique can be used for the production of liquid membranes. However, the risk of contamination of working place with ionic liquids that still lack toxicology data, prohibited the further application of this method.

For tubular and capillary supports, the thin active layer usually covers the inner surface of the tube. Therefore, one possibility to immobilise the liquid in this layer is to fill the support pressureless with it using e.g. pipette (Fig. 5.21b) and to control the duration of the liquid penetration into the pores. A more sophisticated technique, which also allows for the application of protective gas and vacuum is shown in Fig. 5.21c. Yet another method (which was used in IGB and M&H supports) is the infiltration method, where the outer surface of the support is covered with the liquid by applying vacuum from the...
inner side at the same time (Fig. 5.21d).

Figure 5.21: Different methods of liquid membrane preparation a) „brush” method for flat membranes b) „fill” method for membrane tubes c) „syringe” method for capillaries d) „infiltration” method for capillaries

Depending on the support supplier, about 50% of all membranes produced in this way could not found to be „dense” after the first preparation attempt. Even after the second attempt with the same membranes, they did take up almost no additional liquid (less than 0.5 wt.%) and were - again - in more than 75% of cases not dense. This behaviour is typical for ceramic membranes and may be attributed to the „pin holes”, i.e. defects in the active layer of the membrane.

Thinner membranes?

The flux through the membrane can be maximised by the production of as thin liquid films as possible, whereas these should retain their mechanical stability (against transmembrane pressure). In the following, a development of a technique for production of thin liquid membranes is presented.

Since it is much easier to produce uniformly filled membranes by infiltration technique than with other methods, it is reasonable to start with a diluted solution of ionic liquid. The principle of whole procedure is shown in Fig. 5.22.

IL is filled in the pores of the support. Support is attached to the surface of the solvent reservoir. The solvents used can be polar on non polar (methanol and methylene chloride), but must be both removable by vacuum leaving only ionic liquid left in the support. By convection the solvent will evaporate dragging the ionic liquids convectively to the top of the membrane support. At some point the membrane support will detach from the solvent’s surface because the reservoir amount slowly decreases. Finally, we end up with partially filled support. So far the theory. The results of the preparation of real (tubular and flat) supports are shown schematically in Fig. 5.23. The most striking and surprising feature found is the observation of the „sweating” of the ionic liquid or formation of pearls on the surface, especially in the case when polar solvent is used. Non-polar solvent
probably leads to non-visible droplets within the pores, which can not be proven. However, in both cases the produced membranes are not dense, independently of the initial dilution ratio (solvent : IL = 1:1; 1:3; 1:6; 1:9).

The thickness reduction experiments were repeated with non-porous quartz and glass plates. The behaviour could be reproduced even with non-membrane material: small droplets or pearls develop suddenly from homogenously appearing thin layer. Although ionic liquids show very good wettability and compatibility with the polar ceramic supports at first glance, they show very unusual aggregation behaviour. The adhesion forces to the support do not dominate the cohesion forces within the liquid, which are of course of strong electrostatic nature. This is well in accordance with literature data on clathrate formation [286] in ionic liquids.

5.3.2 Stability and stability tests

As mentioned in the introduction, liquid membranes in generally show poor long term stability due to the loss of the separation liquid phase. In previous section I have stated that ionic liquids apparently show excellent wettability of polar ceramic porous supports. This behaviour must be quantifiable in some way. Measurements of appropriate physical properties, i.e. surface and those concerning wetting, and the respective methods will be introduced in the following, that should enable an estimation of the stability of supported liquid membranes used.
5.3. SUPPORTED LIQUID MEMBRANES

The combination of a certain support with a chosen (ionic) liquid determines the mechanical (pressure) stability of liquid membrane. In order to estimate the maximum transmembrane pressure $p_{TM}$ that can be applied to a membrane support with the pore diameter $d$, where the liquid is immobilised exclusively by capillary forces, one has to look closer at the so called Laplace-Young equation\textsuperscript{10} [291, 292]:

$$\Delta p_{TM} = 4K\sigma \cos \theta \frac{1}{d}.$$\textsuperscript{10}

$K$ describes the non-ideality of the pores (tortuosity or curvature factor, usually taken as 1 for straight pores and $\frac{2}{\pi} \approx 0.6$ for sintered particles). The liquid trapped in the pores is characterised by its surface tension $\sigma$ and its wetting angle $\theta$ of the respective support. For surface tension measurement, two methods are applied: pendant droplet method and Du Nouy ring method on dynamic tensiometer. The results for a few ionic liquids are given in Tab. 5.3. For comparison, the surface tension of water at 20°C is found to lie between 72 and 74 mN/m, that of mercury equals 488 mN/m. Molten inorganic salts like NaCl (1073°C), KClO$_3$ (368°C), KNCS (175°C), NaNO$_3$ (308°C) and K$_2$Cr$_2$O$_7$ show surface tension values of 115, 81, 101.5, 116.6 and 129 mN/m, respectively [293]. It has to be noted that the surface tension obtained in this manner holds for the air/liquid interface.

Interestingly, the surface tension of low temperature organic ionic liquids is much lower than that of inorganic melts. Common organic liquids [92] display surface tensions between 20 and 40 mN/m, that is an interval, where ionic liquids clearly fall in. Not unusual

---

\textsuperscript{10}This equation is strongly associated with the term capillary condensation, where surface tension competes with van der Waals forces. For additional information on this complex issue see [287, 288, 289, 290].
is also a slight decrease of surface tension with increasing temperature, which can be attributed to decreasing density of the liquid.

Contact angle is another parameter of interest. It is measured with an optical system, where a fine droplet (up to max. 10 µl) is put onto a given surface thereby forming a solid-liquid-air contact system. Example pictures from measurements for [BMIM]$^+$ [BTA]$^-$ on different supports are shown in Fig. 5.24. Complete results with yet another ionic liquid [BMIM]$^+$ [CuCl]$^2_2$ can be found in Tab. 5.4. It is important to notice, that in most membrane supports, there exist physical property differences between the macroscopic outer membrane surface and microscopic surface being the walls of the pores. This holds in particular for the dendritic Al$_2$O$_3$ membrane, where the solid surfaces belong to different crystallographic habits (planes). Therefore, the values given here must be taken with care. Furthermore, the 20 nm pores on the top wet better than 200 nm pores at the bottom.

![Figure 5.24](image-url)

Figure 5.24: [BMIM]$^+$ [BTA]$^-$: surface tension measurement a) pendant droplet method; evaluation of wetting properties on: b) glass c) stainless steel d) ceramic membrane e) Anodisc membrane (bottom)

The active side of the ceramic membrane (HITK, pore size 5 nm) shows a totally smooth and shiny surface. Wetting is good and comparable to that of Anodisc membranes. It seems that the surface structure and the pore size influences the observable wetting. In case of ceramic supports on woven metal fabric (Creavis membranes, $d=100$ nm),
5.3. SUPPORTED LIQUID MEMBRANES

the liquid is sucked into the support so quickly that it was nearly impossible to take a representative picture for evaluation purposes.

In general, it is desirable for supported liquid membrane applications that the support is completely wetted ($\theta=0$).

<table>
<thead>
<tr>
<th>IL</th>
<th>glass [°]</th>
<th>stainless steel [°]</th>
<th>ceramic membrane [°]</th>
<th>metal woven ceramic m. [°]</th>
<th>Anodisc m. (top) [°]</th>
<th>Anodisc m. (bottom) [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM]$^+$ [BTA]$^-$</td>
<td>38,98</td>
<td>37,33</td>
<td>16,17</td>
<td>(8,50)</td>
<td>14,82</td>
<td>49,73</td>
</tr>
<tr>
<td>[BMIM]$^+$ [CuCl]$_2$</td>
<td>24,08</td>
<td>30,12</td>
<td>23,38</td>
<td>-</td>
<td>36,48</td>
<td>43,87</td>
</tr>
</tbody>
</table>

With this data gathered, it is now possible to calculate the theoretical maximum transmembrane pressure $\Delta p_{TM}$. For ceramic, metal woven and anodisc membranes with [BMIM]$^+$ [BTA]$^-$ are 175, 9 and 59 bar respectively\textsuperscript{11}. In the next sections, stability in terms of transmembrane pressure will be the subject of experimental investigation.

Experiments on membrane stability

In principle, membrane stability can be assessed using three methods, namely bubble point test, liquid displacement test and selectivity test during “real” permeation experiment.

In all tests, increasing pressure of the test gas (usually nitrogen) or gas mixture is applied to the feed side of the supported liquid membrane. In the bubble point test, the membrane is first covered with about 5 to 10 mm of the liquid of interest. When the test gas displaces liquid in the biggest pore, one observes rising bubbles in the liquid. The pressure at which the first bubble is observed is called bubble point. The measurement is usually conducted against ambient pressure. Since the results are more unreliable in comparison to the other two tests, bubble point test was performed on FluxxIon and GAP aluminium metal membrane only (Table 5.5).

In GAP aluminium metal membrane a bubble point with [BMIM]$^+$ [BTA]$^-$ of 770 mbar was found.

In the displacement method, volumetric flow (I used nitrogen as test gas) is measured on the permeate side of the apparatus shown in Fig.5.25. At low transmembrane pressures, only diffusion of the gas through the membrane contributes to the flux. At higher pressures, liquid is firstly displaced from the big pores, then from the medium pores and finally from the small pores. Thus, convective flux plays an increasingly dominant role. As a rule of the thumb, 70-80% of the break point pressure should be used in the separation.

\textsuperscript{11}An experienced membranologist will recognise that these values surpass experimental observations by at least 1 order of magnitude. However, although Laplace-Young equation is obviously not applicable to real world problems, it is constantly cited in the membrane literature [282, 294].
Table 5.5: Bubble point in FluxxIon membranes with [BMIM]$^+$ [BTA]$^-$ in terms of relative pressure, the range relates to several observations

<table>
<thead>
<tr>
<th>pore size $[\mu m]$</th>
<th>bubble point $[mbar]$</th>
<th>bubble point range $[mbar]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>360</td>
<td>340-370</td>
</tr>
<tr>
<td>2.0</td>
<td>520</td>
<td>470-580</td>
</tr>
<tr>
<td>1.2</td>
<td>770</td>
<td>670-900</td>
</tr>
<tr>
<td>0.8</td>
<td>1230</td>
<td>1200-1500</td>
</tr>
<tr>
<td>0.45</td>
<td>1660</td>
<td>1550-1740</td>
</tr>
</tbody>
</table>

Before I describe the results of the stability measurements achieved by displacement method, membrane modules for different membranes used in this work, must be introduced. The same modules, which are an important part of the apparatus, will also be used for the permeation experiments.

**Membrane modules**

A membrane module is actually a chassis for the membranes. For every membrane geometry and for every application an appropriately designed module is necessary. A geometry of the module determines the flow regimes of the feed, retentate and permeate compartment, but this subject is treated elsewhere in detail, e.g. in [23]. Modules used in this work are displayed in Fig. 5.26. Except for IGB and M&H capillaries, where resin is used as sealant, all membranes are fixed into the module by Viton o-rings.

Now I can return to the stability tests by displacement method. As described above, I have tested Anodisc flat membrane and capillary membranes IGB and M&H. The results are presented in Fig. 5.27.

The test liquid used was my standard system [BMIM]$^+$ [BTA]$^-$, in case of Anodisc I have also included ionic liquid ethylpyridinium ethylsulfate, [EP]$^+$ [ES]$^-$ . It can be seen, that in Whatman Anodisc there exists certain basis permeability of the membrane already at low transmembrane pressures. In contrast, capillary membranes seem to be completely...
5.3. SUPPORTED LIQUID MEMBRANES

Figure 5.26: Modules for: a) membrane tubes (HITK, Pall-Schumacher; length \( L \) 100 mm, outer diameter \( d_o \) 10 mm) b) capillary membranes (HITK; \( L = 250 \) mm, \( d_o = 2.9 \) mm) c) flat membranes (Whatman, Creavis; discs \( d_o = 47 \) mm) d) capillary membranes (IGB, M&H; 100 mm < \( L < 250 \) mm, \( d_o < 1.5 \) mm) and e) resin used as sealant

dense. The breakthrough pressures can be clearly determined in all cases to 6.8 bar (Anodisk), 1.9 bar (IGB), 11.5 bar (M&H type A) and 12.1 bar (M&H type B). Thus, operational pressures, which are recommended for the permeation experiments can be determined (for Anodisc, 5.5 bar was used). However, I decided not to conduct any permeation experiments with capillary membranes, since they are very fragile, comparably thick (>180 \( \mu \)m), thus almost non-permeable even at high pressures and finally, difficult to handle in respect to the mounting into the membrane module.

Figure 5.27: Ionic liquid \([\text{BMIM}]^+ [\text{BTA}]^-\) displacement from a) Whatman Anodisc and b) from IGB and two types of M&H supports
5.3.3 Gas and Vapour Permeation experiments

In the preliminary permeation experiments the fluxes and permselectivities were determined in the apparatus already introduced in the Fig.5.25a. The permselectivities are defined as selectivities, which are based on the ratio of fluxes of pure gases and vapours. This is probably the best method for measurement of permselectivity, since the permeation fluxes can be determined easily by adjusting the transmembrane pressure \((p_F, p_P)\), measuring the time and observing the permeated volume.

It is important to notice, however, that the permeate side must be completely purged with the permeating gas before the experiment. Without purging, the permeate compartment is usually filled with air or gas/vapour from previous experiments. Thus, the feed (e.g. pure \(N_2\)) and permeate (e.g. pure \(CO_2\)) compositions being different, one actually encounters a much higher partial pressure difference (initially ca. 1 bar) than shown by pressure transmitters. This phenomenon indeed plays an important role. It was confirmed by the impressive observation, in which the volumetric flow occurs from the permeate side across the membrane back to the feed side even at the feed-side pressure of 3 bar and permeate-side pressure of 1 bar\(^{12}\). The alternative handling of this problem is the application of membrane pump that maintains vacuum (3-10 mbar) and conveys the permeated fluid into the burette. In the experiments, both methods were applied and have given consistent results, which are presented in the following sections. In all experiments that were conducted with gases of technical quality, fully impregnated Anodisc membranes were used.

Separation of Components of Natural Gas

Permeation measurements were conducted with pure gases that were applied in alternating series (e.g. \(CO_2 - N_2 - CO_2 - N_2\)). Results for the ideal separation of components of natural gas are given in Table 5.6.

<table>
<thead>
<tr>
<th>gas</th>
<th>flux (\text{dm}^3\text{m}^{-2}\text{h}^{-1}\text{bar}^{-1})</th>
<th>TMP (\text{bar})</th>
<th>flux (\text{dm}^3\text{m}^{-2}\text{h}^{-1}\text{bar}^{-1})</th>
<th>TMP (\text{bar})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CO_2)</td>
<td>39.8</td>
<td>4.93</td>
<td>3.78</td>
<td>6.57</td>
</tr>
<tr>
<td>(N_2)</td>
<td>2.5</td>
<td>6.43</td>
<td>0.22</td>
<td>5.59</td>
</tr>
<tr>
<td>(H_2)</td>
<td>2.7</td>
<td>6.03</td>
<td>0.32</td>
<td>6.97</td>
</tr>
<tr>
<td>(CH_4)</td>
<td>6.4</td>
<td>6.48</td>
<td>0.26</td>
<td>6.56</td>
</tr>
</tbody>
</table>

The permeability of carbon dioxide is much higher than the permeabilities of methane, hydrogen and nitrogen. Therefore, separation is in principle possible. In case of hydrogen,

\(^{12}\)Here, the total transmembrane pressure difference is 2 bar: the feed-side pressure of pure \(N_2\) is 3 bar, the permeate-side pressure of \(CO_2\) is 1 bar, which are the actual partial transmembrane pressure differences. Since the permeability of \(CO_2\) is of approximately two orders of magnitude higher than that of \(N_2\), the total flux of \(CO_2\) from permeate to feed is higher than that of \(N_2\) in the reverse direction.
5.3. **SUPPORTED LIQUID MEMBRANES**

in spite of its lower solubility in [BMIM]$^+$ [BTA]$^-$ in comparison to the solubility of nitrogen, higher permeation rates were observed. This can be explained by its supposedly higher diffusion coefficient. In the second experiment, where the membrane was prepared with ionic liquid [Et$_2$-BMIM]$^+$[BTA]$^-$ lower overall fluxes were observed for all gases as expected due to the large difference in viscosity. The selectivities can be compared to those obtained in experiments with [BMIM]$^+$ [BTA]$^-$. 

**Permanent Gases - Air separation**

The O$_2$ - N$_2$ system was also measured in the experimental setup shown in Fig. 5.25a. The feed pressures applied were adjusted to 6 bar in all experiments. Permeate was held at ambient pressure. Permeate compartment was purged in each run. Permeate vacuum was not applied. Measurements were performed at ambient temperature (20°C), at 50°C and at 70°C. Before entering the membrane module gas from the gas supply line was heated in a stainless-steel capillary loop to the desired temperature. Permeate flux was measured by gas bubble counter, after it was cooled down to room temperature. The results are shown in the Table 5.7.

Table 5.7: Experimental results for permeabilities of pure oxygen and nitrogen at different temperatures in 60 µm thick SLM prepared by IL [BMIM]$^+$[BTA]$^-$

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>O$_2$ flux [dm$^3$ m$^{-2}$ h$^{-1}$ bar$^{-1}$]</th>
<th>N$_2$ flux [dm$^3$ m$^{-2}$ h$^{-1}$ bar$^{-1}$]</th>
<th>O$_2$/N$_2$ flux-ratio [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>5.76</td>
<td>2.27</td>
<td>2.53</td>
</tr>
<tr>
<td>50</td>
<td>6.81</td>
<td>3.29</td>
<td>2.08</td>
</tr>
<tr>
<td>70</td>
<td>13.83</td>
<td>8.12</td>
<td>1.7</td>
</tr>
</tbody>
</table>

The permselectivity decreases with increasing temperature, whereas the total flux increases. This particular case shows that it is the solubility, which does play more decisive role for the better selectivity. Because of the negligible difference in diffusion coefficients of oxygen and nitrogen in IL the diffusivity has a lower impact. This experimental observation also confirms the trend that was observed in mass transport modelling chapter, where the selectivity corresponds to the ratio of Henry coefficients obtained by e.g. COSMOtherm method. The diffusion coefficient increases with increasing temperature, but for both species equally, thus influencing only the total flux but not the selectivity.

**Separation of Propane and Propylene**

Permeation experiments with propane and propylene were performed with a few of the available ionic liquids. Each experiment was repeated 3 times with the Whatman inorganic support (in case of leakage, the support was repeatedly impregnated with the respective IL). The results (mean values) of these measurements are presented in Table 5.8. Extraordinary high permselectivity in case of ionic liquid [EMIM]$^+$ [EtSO$_4$]$^-$ must be attributed to the unknown experimental error. In all other cases, propylene permeates through the
membrane slightly better than propane. However, significant separation factors are not achieved.

Table 5.8: Permeabilities of pure propane and propylene in SLM prepared by different IL in 60 µm thick SLM at room temperature

<table>
<thead>
<tr>
<th>IL</th>
<th>Propylene flux [dm$^3$ m$^{-2}$ h$^{-1}$ bar$^{-1}$]</th>
<th>Propane flux [dm$^3$ m$^{-2}$ h$^{-1}$ bar$^{-1}$]</th>
<th>Flux-ratio [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM]$^+$ [BTA]$^-$</td>
<td>9.76</td>
<td>3.33</td>
<td>2.93</td>
</tr>
<tr>
<td>[OMIM]$^+$ [Br]$^-$</td>
<td>6.39</td>
<td>3.03</td>
<td>2.11</td>
</tr>
<tr>
<td>[HMIM]$^+$ [PF$_6$]$^-</td>
<td>2.34</td>
<td>0.47</td>
<td>4.98</td>
</tr>
<tr>
<td>[IP-PW(C)]$^-$</td>
<td>2.98</td>
<td>2.54</td>
<td>1.17</td>
</tr>
<tr>
<td>[MOPy]$^+$ [BTA]$^-</td>
<td>33.4</td>
<td>22.04</td>
<td>1.51</td>
</tr>
<tr>
<td>[EMIM]$^+$ [EtSO$_4$]$^-</td>
<td>1.52</td>
<td>0.11</td>
<td>13.82</td>
</tr>
</tbody>
</table>

5.3.4 Lab-scale membrane vapour permeation plant

Whereas above I have used a simple equipment for determination of permselectivities and fluxes, which can be used for screening purposes, for the „real world” approach the selectivities of a feed mixture have to be measured. Again, propane-propylene separation is focused. The standard system with ionic liquid [BMIM]$^+$ [BTA]$^-$ was applied. Some additional experiments were performed using the promising membrane phase liquid [BMIM]$^+$ [CuCl$_2$]$^-$. The permeation apparatus with the module designed for capillary membranes (HITK) is shown in Fig. 5.28.

In this system, it is possible to variate the operating feed pressure up to 5 bar and the temperature of the module up to 60°C. Module is electrically heated and insulated by glass wool. Isothermal conditions are controlled by the on-line measurement of the temperature.

In all experiments, pure nitrogen is used as a sweep gas (10 ml/min) at the permeate side (1 bar) and a propane/propylene mixture supplied in 1:1 ratio as a feed (4 ml/min) throughout the experiments. Although permeate and feed side can be reversed by switching the valves V3 and V4 (Fig. 5.28), the inner compartment of the membrane is treated here as the feed side (the side of the membrane with active layer). Permeate and retentate streams exiting the back-pressure valve expand towards ambient pressure. Both streams can be analysed in a gas chromatograph. Knowing the flow rates and the concentrations of the entering and exiting streams it is possible to calculate the permeation rate by applying a simple integral balance equation.

Pressure Stability Tests

The apparatus described previously may be used for the pressure stability tests. In these tests [BMIM]$^+$ [BTA]$^-$ was used with HITK capillary membrane (pore size 5 nm) at ambient temperature. The feed used was 1:1 propane/propylene mixture. The results
5.3. SUPPORTED LIQUID MEMBRANES

from two typical experiments, where the permeability and selectivity is monitored with increasing pressure, are shown in Fig.5.29.

Figure 5.29: Pressure stability tests: a) propane and propylene permeation rate vs. pressure b) selectivity (ratio of „real” permeation rates) vs. pressure

A slight trend towards lower propylene and propane permeability at higher pressures is
observed. In both experiments permeability of each vapour approaches an almost constant plateau above 3.5 bar. The logical permeation trend would be a higher permeability with increasing pressure, since the increasing working pressure implies higher solubilities, hence higher driving force and therefore higher permeate flow. However, it seems that some concentration polarisation effects play an important role. With increasing pressure, the selectivity also decreases. For propane/propylene this can be considered to be logical: the more „critical” a gas or vapour becomes, the lower is its differential solubility. It can be concluded that membrane stability is given up to transmembrane pressures of 3.5 bar. The reasonable operating pressure taking into account an empirical security factor can be then set to approximately 2.5-3 bar.

**Long-Term Stability Tests**

Long term stability was tested at constant feed pressure of 2.5 bar and at ambient temperature. The feed is 1:1 mixture of propane/propylene. The results of the experiments are presented in Fig. 5.30.

![Figure 5.30: Long term stability in terms of: a) propane and propylene permeation rate b) selectivity (ratio of „real” permeation rates)](image)

Looking at the permeation rates, almost constant values for both components can be observed over a day of operation. The selectivity, expressed as the ratio of „real” permeability rates, surprisingly increases with time. For this behaviour I cannot provide an appropriate explanation. Furthermore, shortly after the achievement of maximum selectivity, the selectivity drop is observed after 20 hours of operation. It can be concluded that the operation is stable long enough for the purpose of the separation evaluation.

**Permeation experiments**

So far, I have presented methods for testing stability of the produced liquid membranes. However, at the same time, these tests also serve as permeation experiments, which enable the determination of selectivity and fluxes as this was demonstrated for the case of \([\text{BMIM}]^+ [\text{BTA}]^-\) above.
5.4 Usage of Carriers in SLM with ILs - Solubility

I wish to present here the study of another system, i.e. [BMIM]$^+$ [CuCl$_2$]$^-$, which has been already treated from different points of view. A capillary ceramic support (HITK) with an active layer of 5 nm mean pore size was treated with the ionic liquid in a preparation setup according to Fig. 5.21c. The membrane was build into the module and the feed mixture was introduced to the inside of the capillary membrane with a flow rates from of 4.1 to 4.23 ml/min. The feed-side pressure was set to 2.5 bar, whereas the permeate-side was at pressure of 1 bar. Nitrogen sweep was introduced at 10 ml/min. Permeation experiments were conducted at membrane module temperatures of 20, 40, 60 and 80°C. The piping to the gas chromatograph was held at 30°C. The results of the experiments are presented in Fig. 5.31.

![Figure 5.31](image_url)

Figure 5.31: Permeation rates and selectivity (expressed in ratio of „real” permeation rates) in propane and propylene separation experiments using [BMIM]$^+$ [CuCl$_2$]$^-$ system at a) constant temperature (an average of 3 GC values) and during b) cooling down phase (only one GC measurement per hour)

Again, higher permeability values of propylene compared to those of propane are observed: propylene permeability is around three times higher than propane permeability. With these values, calculated „real” selectivity is the highest observed selectivity among the treated systems so far, which also could be confirmed in reproducible experiments. In agreement with the well with known trends, permeability increases with increasing temperature. At 20°C, the stable values of propylene and propane permeability - as estimated from the integral mass balance - are 3.34 and 1.07 1/(m$^2$ bar h), respectively. At 80°C propylene permeability reaches 19.19 1/(m$^2$ bar h) and that of propane 6.87 1/(m$^2$ bar h). Selectivity thus decreases from 3.1 to 2.8. Interestingly, when the system is cooled from 80°C down to the ambient temperature, the permeability decreases to the initial value, whereas selectivity increases accordingly and even slightly surpasses the initial value.

5.4 Usage of Carriers in SLM with ILs - Solubility

In the thesis’ introduction I have stated that carriers can be also considered as catalysts, since they do not chemically change during facilitated transport. In principle, as within
catalysis in general, two approaches of carrier usage are possible: carriers can be homogenously dissolved or heterogeneously suspended in ionic liquids. In this work I have attempted both approaches, which are presented in the next sections.

5.4.1 Homogeneous Approach

The first attempts of carrier application were made with typical compounds known from other membrane applications. For instance, for enhancing the solubility of carbon dioxide, amino acid glycine and its sodium salt, glycinate were tested with two ionic liquids ([BMIM]$^+$ [BTA]$^-$ and [EtPy]$^+$ [EtSO$_4$]$^-$). Unfortunately, both compounds are either not soluble$^{13}$ or react with the solvent according to the reaction scheme shown in Fig. 5.32. Solubility was tested under vigorous stirring or application of ultra sound accompanied by enhancement of the temperature. Dissolving inorganic salts proved to be difficult for all ionic liquids in general - several experiments were undertaken and most ended with purely biphasic liquid-solid systems (Fig. 5.32c). On the one hand, this is surprising, since one would believe that „similia similibus solvuntur” (alchimistic „similar dissolves similar”), on the other hand one has to look at the lattice energies of inorganic compounds that lie well beyond 600 kJ/mol $^{[92]}$ in order to realise that this energy has to be brought into the system by solvent interacting with dissociated matter.

![Figure 5.32: Glycine in ionic liquids: a) reaction scheme for pyridinium based IL and b) reactants and products of the reaction c) photograph of precipitated salt AgNO$_3$ in [BMIM]$^+$ [BTA]$^-$ after application of ultra sound](image)

For enhancing the solubility of oxygen, the simplest form of Co-Salen was synthesized (without amine-based proximal base, the coordination was provided by water, some coordination effects of the ionic liquid are also expected). The activity of the product was tested using the solid compound by thermal cycling in the apparatus used for absorption-desorption experiments with ionic liquids (cf. Fig. 5.7)$^{14}$. One such cycle is presented in Fig. 5.33. Solid compound was evacuated, whereas the pressure of below 5 mbar were

$^{13}$Interestingly however, is that compounds that do dissolve in ionic liquids at enhanced temperature, e.g. ammonium nitrate, NH$_4$NO$_3$, precipitate by lowering the temperature in extremely dispersed manner, i.e. in form of very fine crystals.

$^{14}$The adsorption-desorption procedure for ionic liquids requires at least 25 g of ionic liquid. In the experiment with solid Co-Salen compound 16.5 g of pure material were used.
achieved. First, nitrogen was introduced and almost no absorption was observed. After repeated evacuation, oxygen was introduced followed by immediate and rapid adsorption, which was almost completed in 1 hour. Desorption by simple pressure reduction (at 40 mbar) was not successful. If fact, it was marginal by an overall pressure increase of around 40 mbar. Desorption could be, however, reversed by enhancing the temperature to 100°C. The heat transfer in the experimental setup was rather slow, therefore it could not be guaranteed that the temperature shown in Fig. 5.33b, which was measured at the entrance of the vessel really corresponds to the temperature in the vessel. One can nevertheless see that, complete desorption is more easily, i.e. faster achieved than the absorption. Holding the level at 100°C, desorption progressed as far as the beginning pressure minus that of desorption at low pressure. After switching off the heating supply, an adsorption took place again, fast pressure decline is observed at temperatures lower 40°C (this temperature is more accurate because of the relatively high heat capacity of the system). Thus, this experiment proved a very high activity of the compound (more than 90% of oxygen could be absorbed).

![Graphs showing absorption and desorption cycles](image)

Figure 5.33: Absorption and desorption cycle on solid Co-Salen: a) oxygen and nitrogen adsorption at room temperature b) reaction scheme for pyridinium based IL c) photograph of precipitated salt in [BMIM][BTA] after application of ultra sound

The active form could be well dissolved in ionic liquid [BMIM][BTA], whereas a saturated solution was produced by filtering of the ionic liquid through the access of the solid using the finest ceramic laboratory (G4) filter. The filtering yielded an extremely viscous solution and at the later point (when the product was removed from the absorption vessel) even a slurry was observed. Such a segregated product is shown in Fig.5.34a. Furthermore, otherwise low viscous ionic liquid, which behaves as Newtonian fluid, also changed its rheological properties: it not only became more viscous but visibly displayed some structure effects (filamentous behaviour).

In the tested solution (40 g) having approximate ionic liquid to carrier ratio of 1:1, it was shown that Co-Salen, which is easily synthesized, almost completely deactivates in the given ionic liquid. The oxygen absorption in this system is shown in Fig.5.34b. Here, the absorption capacity is comparable to those observed in neat ionic liquid, which are unfortunately not sufficient for effective air separation.
In the chapter on molecular modelling I have presented the Vasca compound. Although the compound is costly and therefore probably not suitable for large scale separation operations, I tried to dissolve the bis-(triphenylphosphine) based material in several ionic liquids. Unfortunately, without success. Among scientists working in the field of catalysis in ionic liquids, the phenomenon of difficulties with dissolving non-polar catalysts in ionic liquids is well known today. Sulfonated aryl compounds, which have been shown to be soluble in some cases, are proposed to be used. However, most of the catalysts in sulfonated form, which would be required in this work, are neither commercially available nor can be easily synthesized.

Conclusion: The deactivation of Co-Salene may be attributed to the dimerisation or oligomerisation of the Co-Salen molecules. The involved agglomeration reactions lead to products, which increase the viscosity of the mixture. It became known later that the coordination ability of the anion $[\text{BTA}]^-$ is not as low as was initially expected. The anion probably coordinates the central metal atom with the free electron pair on nitrogen. More different ionic liquids should be screened in order to find an appropriate anion that both dissolve and weakly coordinates the carrier not deactivating it at the same time. Especially $\text{BF}_4^-$ and $\text{PF}_6^-$-based ionic liquids should be examined. The dilemma of choosing the right solvent can be formulated as follows: weak coordination might not be sufficient for dissolving the carrier (catalyst) but might be already too high for the active site of the carrier. Ionic liquids still represent an unexplored area in the field of catalysis. There are very few heuristic rules about the behaviour of ionic liquids, if any. In this sense a lot of „trial and error” work is still ahead.

For enhancing the solubility of propylene, the dissolution of known carrier salts for propylene $\text{AgCl}$, $\text{AgBF}_4$ and $\text{AgNO}_3$, $\text{CuCl}$ was tested in available ILs. Throughout the experiments it was observed that the lattice energy of inorganic salts is too high for IL’s solvation power. Hence, the solubility of inorganic salts in ionic solids is not given (cf. Fig. 5.32c). In the experimental procedure, approx. 5 g of the ionic liquid and 1 g of the corresponding salt were taken. After ultra-sound treatment the suspension was filtered. The filter cake was washed with either dichlormethane in a separate vessel and weighted. Both filtrate solutions were joined, evacuated and finally weighted. From the observations of the checked systems, it can be stated that the overall solubility is less that 0.1 wt.%. 

Figure 5.34: Co-Salen-[BMIM]$^+$ $[\text{BTA}]^-$ combination: a) the solution (slurry) b) oxygen absorption
This amount is far below the desirable concentration of the carrier, which has been taken into account as realistic value in the theoretical part of this work (approx. 1 mol per liter, 20 wt.%).

The second group of tested olefine carriers are acetylacetonates of nickel, platinum and palladium. Among the three compounds, only Pt(acac)$_2$ is sufficiently soluble (approx. 10 wt.%) in [BMIM]$^+$ [BTA]$^-$ to be taken for the permeation experiments. In the further experiments it was attempted to combine [BMIM]$^+$ [BTA]$^-$ with CuAlCl$_4$ and [BMIM]$^+$ [CuCl$_2$]$^-$ with AgNO$_3$. In the former case a gel-like substance was obtained. In the later, an exothermic reaction took place with apparently undefined product spectra, which however proved to be nonvolatile and liquid. Here in both cases the membrane preparation was possible.

5.4.2 Heterogeneous Approach - Molecular Clusters

In particular, hydrogen solubility in ionic liquids is very low. Experimental evidence so far shows that it cannot be significantly enhanced by simply changing the functional groups of ionic liquids [295]. Hydrogenation reactions in ionic liquids are therefore usually conducted under pressures up to 100 bar. In case of hydrogen, there exist almost no appropriate carrier compounds as they are known for oxygen or olefins. An exception might be metallic nickel and even more metallic palladium. Recently, some more complicated inorganic cage-like structures were reported for hydrogen storage [296]. Especially palladium is known for ability to absorb up to 900 times its own volume in hydrogen. This fact is used in dense palladium membranes, which are already used for separation of hydrogen from other gases. Their advantages are high selectivity and high achievable fluxes due to the selective dissociative adsorption and high mobility of hydrogen atoms within the palladium lattice$^{15}$. In order to enhance the affinity of an arbitrary IL and to increase the hydrogen flux through the supported liquid membrane, clusters of black palladium might be utilised for this purpose. Nanocluster approach was already reported for polymer films [297]. In the following, tests on combination of ionic liquid and elemental palladium are reported. Some work in the context of membrane reactors was also published [48]. In our setup, palladium nanoclusters arranged in the ionic liquid should have the function of more or less immobile carrier (hopping mechanism).

**Preparation** To get the palladium clusters into the ionic liquid, first a suitable palladium precursor must be synthesised. I used ($\eta^3$-allyl)($\eta^5$-cyclopentadienyl)palladium(II) compound (cf. C), which was already used in palladium membrane preparation [28]. The precursor was dissolved in the IL [BMIM]$^+$ [BTA]$^-$. Then, a membrane was impregnated with the mixture of ionic liquid and palladium unreduced complex. Finally the membrane phase was reduced in situ (in the membrane) with hydrogen to yield metallic palladium. In the separate experiment without membrane, the solution containing the precursor was bubbled with hydrogen. In both cases, organic material was removed by evacuation. Palladium metal clusters appeared glowing green at first. However, after approx. 1 hour the

$^{15}$However, palladium membranes must be activated at around 300°C in order to preform the separation. This activation can not be done in ionic liquids that readily decompose around 250°C.
solution turned dark brown and the next day black palladium precipitated in the flask. The results from in situ membrane preparation are shown in Fig. 5.35.

As supports, Creavis and Whatman membranes were used. In each case, the membranes became black-grey while the pores were filled with palladium(0). In order to find out the activity of the obtained nano-suspensions, the system was submitted to solubility measurement as this was done before for Co-Salen. Unfortunately, I could not observe any increased uptake for hydrogen over the system without Pd(0)-carrier. This might be due to the low concentration of the carrier, which do not visibly change the hydrogen solubility of the liquid. Another effect that may occur is the formation of clathrate-like structures. Clathrate cages may limit the transport of hydrogen to the surface of the clusters. In many cases (e.g. absorption of carbon dioxide by caustic solutions), the reaction enhances mass transport through the diffusion layer. This is here apparently not the case.

So far, the cluster system proved not to be a good solution for the separation of hydrogen from gas mixtures in supported liquid membranes. Certain intrinsic solubility must be given in order to enable the contact to the active sites within the liquid. Since solubility of hydrogen is already low, the uptake will also be limited.

There might, however, be an advantage of the low hydrogen solubility in ionic liquids. This is the case, when components other than hydrogen are desired to be separated from hydrogen mixtures. The feed stream, which enters and leaves the membrane module at high pressure, is depleted with respect to other components, whereas hydrogen remains on the high-pressure level and can be then compressed for final application at lower costs, if required.

\[ \text{Pd} + \text{H}_2 \rightarrow \text{Pd}^{++} \]

[I have shown above that permeation of acidic gases, CO\textsubscript{2} in the neat IL is higher than that of hydrogen.]

Figure 5.35: Preparation of palladium clusters: a) reaction scheme b) membrane appearance before and after palladium preparation
5.4. USAGE OF CARRIERS IN SLM WITH ILS - SOLUBILITY

5.4.3 Selectivity Measurements with Carrier Approach

Finally, selectivity measurements of the membranes produced with either solutions or suspensions of carriers from the previous section are reported. The permselectivities for oxygen/nitrogen separation with Co-Salen for what I believed to be the best separation temperatures are presented in Table 5.9.

Table 5.9: Permselectivities for oxygen/nitrogen separation in SLM prepared by Co-Salen containing IL

<table>
<thead>
<tr>
<th></th>
<th>O₂-flux [dm³ m⁻² h⁻¹ bar⁻¹]</th>
<th>N₂-flux [dm³ m⁻² h⁻¹ bar⁻¹]</th>
<th>flux ratio [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM][BTA]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoSalen (saturated)</td>
<td>2.88</td>
<td>1.36</td>
<td>2.12</td>
</tr>
<tr>
<td>70</td>
<td>4.25</td>
<td>2.47</td>
<td>1.72</td>
</tr>
<tr>
<td>[BMIM][BTA]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoSalen (half saturated)</td>
<td>2.23</td>
<td>0.92</td>
<td>2.43</td>
</tr>
<tr>
<td>70</td>
<td>5.15</td>
<td>1.6</td>
<td>3.21</td>
</tr>
</tbody>
</table>

The usage of carrier, independent of its concentration - neither half saturated nor saturated Co-Salen in [BMIM][BTA] did not show any advantage over the simple membrane prepared with neat IL. As stated above, by dissolving Co-Salen in IL [BMIM][BTA] the viscosity of the solution is greatly enhanced: both oxygen and nitrogen fluxes in these „carrier” membranes were significantly lower than in the membrane without carrier. The difference in viscosity influences the diffusion coefficient and makes it difficult to directly compare the results. However, more importantly, the selectivity could not be improved.

The results for propane/propylene separation with the usage of carriers are gathered in the Table 5.10.

Table 5.10: Selectivities for propane and propylene separation in SLM prepared by IL saturated with the respective carrier at room temperature if not stated otherwise

<table>
<thead>
<tr>
<th></th>
<th>exp. runs [-]</th>
<th>vol.% C₃H₆ [-]</th>
<th>vol.% C₃H₈ [-]</th>
<th>ratio [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM][BTA]</td>
<td>10</td>
<td>14.28</td>
<td>7.83</td>
<td>1.83</td>
</tr>
<tr>
<td>&amp; CuCl</td>
<td>2</td>
<td>2,60 (3.23)</td>
<td>2,60 (3.32)</td>
<td>≈1</td>
</tr>
<tr>
<td>[BMIM][CuCl₂]</td>
<td>6</td>
<td>0.30</td>
<td>0.13</td>
<td>2.38</td>
</tr>
<tr>
<td>&amp; AgNO₃</td>
<td>6 (60°C)</td>
<td>0.91</td>
<td>0.45</td>
<td>2.04</td>
</tr>
<tr>
<td>[BMIM][CuCl₂]</td>
<td>11</td>
<td>0.97</td>
<td>0.56</td>
<td>1.73</td>
</tr>
<tr>
<td>&amp; AgNO₃</td>
<td></td>
<td>5.68</td>
<td>5.56</td>
<td>1.16</td>
</tr>
<tr>
<td>[BMIM][CuCl₂]</td>
<td>6 (60°C)</td>
<td>27.95</td>
<td>16.99</td>
<td>1.61</td>
</tr>
<tr>
<td>&amp; Pt(acac)₂</td>
<td>10</td>
<td>16.35</td>
<td>10.46</td>
<td>1.48</td>
</tr>
<tr>
<td>[BMIM][CuCl₂]</td>
<td>3 (40°C)</td>
<td>15.76</td>
<td>11.06</td>
<td>1.43</td>
</tr>
<tr>
<td>&amp; Pt(acac)₂</td>
<td>6 (60°C)</td>
<td>21.65</td>
<td>12.78</td>
<td>1.61</td>
</tr>
<tr>
<td>[BMIM][BTA]</td>
<td>27</td>
<td>12.12</td>
<td>8.70</td>
<td>1.37</td>
</tr>
</tbody>
</table>

If values obtained in experiments with carriers are compared to those obtained in mem-
branes with neat liquids, no improvement of selectivity is observed. Actually, the selectivity is even lower. This may be due to the low carrier solubility on the one hand, but also due to the deactivating effect of ionic liquids. The already mentioned, option of the clathrate formation around the active site, which decreases the effective diffusion coefficient to the catalyst, is also possible. The only effect that may have (however irrelevant) significance is the Pt(acac)$_2$ system at 60°C that shows an increase of the selectivity with higher temperature.

5.5 Additional issue: Diffusion coefficients

There are principally three possibilities to determine diffusion coefficients: through molecular dynamics (MD) simulation, by usage of empirical relationships and experimental measurements.

Time consuming MD simulation, which I have personally found both tedious and non-trivial, was performed in Chapter 4 with unreliable and quite divergent results. MD is actually non-adequate for routine engineering use. Empirical relationships including incremental methods are widely used in engineering practice with satisfying results for common (liquid/liquid and gas/liquid) systems [16, 116]. The problems arise, when one has to apply the published procedures to new liquid compounds, in my particular case to ionic liquids. Apart from unknown increments, one still needs some initial physical data in order to use them. In such case experiments must be performed. The experimental determination of diffusion coefficients is, however, a delicate task, because it is difficult to completely eliminate free convection within the liquid.

I wish to present two methods for experimental determination of diffusion coefficients, both based on the same line of reasoning. Since the free convection is highly suppressed within the porous supports, its contribution is not expected to falsify the pure diffusion. Therefore, it is reasonable to use porous supports, i.e. membranes for immobilising the liquid subjected to the measurements.

5.5.1 Diffusion and permeation

It is possible to perform permeation experiments and then to calculate the diffusion coefficients [113] from the permeation rate, solubility and thickness of the permeation layer according to:

\[ D_i = \frac{H_i \delta p}{RT} \cdot Q_i, \]

where \( D \) is the diffusion coefficient of the gas or vapour i, \( H_i \) its Henry coefficient, \( \delta \) the support thickness, \( p \) and \( T \) the pressure and temperature on the permeate side and the \( Q_i \) the measured flux of the gas or vapour. Such assessment of data is only possible in membranes with perfectly defined thickness, porosity and in special cases tortuosity. In the Table 5.11, the calculated diffusion coefficients for different gases are presented using two types of membranes, both incorporating the ionic liquid [BMIM]$^+$ [BTA]$^-$. 
Table 5.11: Diffusion coefficients of different gases in [BMIM]$^+$ [BTA]$^−$ assessed by permeation experiments through two types of membranes

<table>
<thead>
<tr>
<th></th>
<th>diffusions coefficient $D_i / \left[10^{-9} \cdot \text{m}^2/\text{s}\right]$</th>
<th>Whatman</th>
<th>Creavis</th>
</tr>
</thead>
<tbody>
<tr>
<td>gas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{N}_2$</td>
<td>$0.110 \quad 1.865 \quad 0.051 \quad 0.133 \quad 0.249$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>$0.727 \quad 8.722 \quad 0.444 \quad 1.535 \quad 2.581$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_4$</td>
<td>$- \quad - \quad 0.054 \quad 0.096 \quad 0.228$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>$0.302 \quad 1.484 \quad 0.195 \quad 0.441 \quad 0.881$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>$0.085 \quad 0.104 \quad 0.079 \quad 0.089 \quad 0.106$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is obvious that the diffusion rate increases with increasing temperature. All acquired data lies in the order of magnitude, where typical values for diffusion coefficients of gases in liquids are expected, i.e. between $10^{-9}$ and $10^{-10}$ m²/s. Hydrogen shows the highest mobility and CO₂ the lowest, confirming that the molecule radius does play an important role. Unfortunately, the values obtained, let say at 20°C, are not the same. The values are, nevertheless, well in accordance with published results [298] based on the similar method (time-lag technique).

5.5.2 Diffusion and absorption

Here, I would like to present another self-developed method for the assessment of diffusion coefficients, where for the prevention of the convective transport the Anodisc support was used. The method uses principally an equivalent setup as was introduced for the absorption-desorption measurements for the determination of Henry coefficients. The main difference are much smaller dimensions of the inner of the cell. The pressure decrease in the cell corresponds indirectly to the diffusion process. The experimental setup and the apparatus’ cell are shown in Fig. 5.36.

The volume of the gas/vapour phase was determined to be 1700 µm (includes the pipe to the valve). In the Anodisc membrane, where the diffusion length is 60 µm, about 45 mg of ionic liquid can be immobilised. The liquid’s amount must be determined individually for each experiment. The measurements of the pressure decrease with time must be performed first in the empty cell as well as in the cell with not loaded support. This must be done in order to account for the absorption of the cell walls and of the pure alumina support. These corrections must be subtracted from the pressure decrease with loaded cell. At the beginning of the experiment, the concentration of gas/vapour in the liquid phase is zero. To prevent the effect of ambient pressure, the starting pressure in the cell is approximately 1 bar\(^1\). It is important to notice that at the phase boundary Henry’s law is assumed. Since the pressure decreases with time, the concentration on the phase

\(^1\)Several experiments using syringe for introducing gas/vapour at up to 800 mbar into the cell, failed because of insufficiently tight septa.
Figure 5.36: Test cell for diffusion measurement by absorption in ionic liquid, immobilised in Whatman membrane: a) setup b) body c) scheme of the apparatus from the inside

boundary is also a function of time. Therefore, for the evaluation and determination of diffusion coefficients (with corrections that are accounted for in the same way) the non-stationary diffusion process according to the second Fick’s law must be used:

\[
\frac{\partial c(z_i)}{\partial t} = D \frac{\partial^2 c(z_i)}{\partial z^2}.
\]

The equation was solved numerically for discrete values of diffusion time \((t_j)\) and diffusion length \((z_i)\), therefore the approximation can be applied

\[
\frac{c(z_i, t_j + \Delta t) - c(z_i, t_j - \Delta t)}{2\Delta t} = D \frac{c(z_i - \Delta z, t_j) - 2c(z_i, t_j) + c(z_i + \Delta z, t_j)}{\Delta z^2},
\]

when sufficiently small values for \(\Delta t\) and \(\Delta z\) are used. The details of the Matlab implementation routine are given in [115].

It turned out that the absorption behavior of ionic liquid changes dramatically when contacted with support. Therefore, Henry’s coefficients as determined in the neat liquid can not be applied (if they are applied in a calculation, they lead to much higher absorption capacity, i.e. pressure drop, than is actually observed with the support in this arrangement). I have decided to manipulate the Henry coefficients is such a way that they fit the
5.6. SUMMARY

experimental pressure drop with the time. The simultaneous least square minimisation of diffusion coefficients in order to fit the data yield the desired result, when the assumption is made that absorption capacity does not influence the diffusion process\textsuperscript{18}. The results from at least four successful measurements per gas/vapor are gathered together in Table 5.12.

Table 5.12: Diffusion coefficients and Henry’s constants by absorption method

<table>
<thead>
<tr>
<th>gas/vapour</th>
<th>$T$ [°C]</th>
<th>$D$ [$10^{-10} \cdot m^2/s$]</th>
<th>$H$ [mbar $\cdot m^3/mol$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon dioxide</td>
<td>25</td>
<td>4.73</td>
<td>81</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>35</td>
<td>12.43</td>
<td>134</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>45</td>
<td>16.34</td>
<td>292</td>
</tr>
<tr>
<td>nitrogen</td>
<td>25</td>
<td>2.97</td>
<td>87</td>
</tr>
<tr>
<td>propane</td>
<td>25</td>
<td>3.74</td>
<td>42</td>
</tr>
<tr>
<td>propylene</td>
<td>25</td>
<td>4.37</td>
<td>35</td>
</tr>
</tbody>
</table>

5.6 Summary

The development of liquid membranes with and without carriers that are based on ionic liquids is still in a very early stage. The materials as well as molecular (catalytic) systems are yet to be systematically characterised in order to be used as being in a tool box for an engineer wishing a development of a working system, which just have to be optimised. Ionic liquids are really a very new class of compounds. They behave very differently in comparison to common industrial solvents. The very special feature of ionic liquids is the negligible vapour pressure. However, even on molecular level, one encounters phenomena of agglomeration and clathrate formation that is so far known only for a few solvents (like water). It is assumed that ionic interactions change entire catalytic chemistry because of not yet known coordination patterns. It is often overseen that the chemistry, in particular chemical kinetics, must be completely redefined in this respect.

It can be summarised that ionic liquids used in this thesis behave as Newtonic liquids except at very low shear rates. This fact and the already mentioned clathrate formation might be the cause for unreliable and experimentally difficult assessment of diffusion coefficients. The density of ionic liquids is usually higher than that of common solvents.

Optical properties of ionic liquids like the index of refraction have not been measured so far. In this work, some data is reported. There is no reliable correlation for calculating permittivity of ionic liquids. The measurement of this quantity gave very scattered results within an extremely broad window of values. Relative permittivity is used in quantum chemical models in order to mimic solvent behaviour. Profound work on this topic is yet to be performed in order to be able to calculate reactivity in ionic media in this way, since

\textsuperscript{18}This assumption might appear odd at first, but after all, the interaction of absorbed species with the walls of support must be diffusion limited, since the capacity is not enhanced.
the concept of ionic strength does not apply to ionic liquids. It is also possible that the continuous solvation models will have to be completely redefined. In unfavourable case, explicit quantum chemistry models with periodic boundary conditions and large numbers of molecules per unit cell for sufficient description of molecular environment will have to be applied in the future.

Solubility of gases, on the other hand goes in line with the observations in classical solvents. The solubility decreases with increasing temperature. The solubility of more polarisable solutes is higher of those with harder electron shell. This can be seen on both examples treated in this theses: oxygen is better soluble than nitrogen, propylene better than propane. In the ionic liquids used, no chemical interactions with solutes were observed. Future work should concentrate on task specific ionic liquids that would be able to undergo such interactions.

On the market, there is a variety of inorganic supports available. None of them have so far been used for immobilisation of ionic liquids. Although strong interactions of ionic liquids with the inorganic supports are expected, the behaviour can not be unambiguously explained. The surface tension of ionic liquids is slightly above organic solvents, the wetting of the supports is comparably good. In spite of these facts, the hold up pressure of liquid membranes in bubble-point and in breakthrough experiments is not as high as expected. It seems that intermolecular ionic forces dominate over the adhesion forces.

In permeation experiments, the selectivities were observed, which were well in accordance with the solubilities of gases/vapours in the ionic liquids. Diffusion coefficients do not seem to play an important role. In order to enhance selectivities, future endeavours must be, again, directed towards task specific ionic liquids. The fluxes through the membrane are yet to be maximised. This can only be realised by making the membrane layer as thin as possible. The thickness of liquid membranes however, depends on the thickness of the support immobilising the liquid. So far, no stable supports thinner than 60 µm are available on the market. The adhesion forces of the supporting material should be enhanced. The only way of cheaply achieving the desired enhancement is the usage of charged material, e.g. ion exchange resin. However, organic matrices show the the problem of swelling. That is why in this thesis only inorganic materials were applied. There is a potential in the further development of silicon based supports, which, however, have to have a functionalised surfaces in order to sufficiently interact with ionic liquids. These supports might also be thin enough and may be the subject of scale-up if only can be shown that sufficient stability can be achieved on the small scale.

The carrier concept in ionic liquids requires a soluble carrier that does not deactivate. Two problems were observed in this work. On the one hand, the common ionic salts are not soluble in ionic liquids to such an extent that they can be used as carriers. The solubility of the carriers should lie about 1 mol/kg or more. Chelate complexes dissolve well in ionic liquids but are prone to coordination of the active site by ionic liquids (especially by the electron reach anions) and thus to deactivation. Again, chemistry must be adjusted to the separation problem in question. A heterogeneous concept of nanoparticulate catalyst was also considered. According to clathrate theory, the diffusion through the cage might be prohibitive for this concept to work efficiently. New carrier concepts must be developed. Special focus should be on the development of self-protecting
carriers and weakly coordinating ionic liquids, i.e. ionic liquids that coordinate enough to serve as a solvent but do not coordinate the active centers of the catalysts.

The reliable measurements of diffusion coefficients are difficult to perform even in common systems due to the free convection, which has to be prevented. A nanoporous supports that immobilise ionic liquids offer an ideal means to prevent this undesirable molecular movement. The modified time-lag and a new absorption based method were used in this work for the determination of diffusion coefficients. Diffusion coefficients of gases and vapours in ionic liquids are an order of magnitude lower than in common organic solvents. In the future, I propose state-of-the-art NMR measurements of the diffusion coefficients.
6 Summary and outlook

This thesis attempts a complete coverage of theoretical and experimental approaches necessary for the development of the separation process of gases or vapours by the means of supported liquid carrier membranes based on ionic liquids.

6.1 Summary

In the first theoretical part, state-of-the-art finite elements simulation software has been used for the mass transport modelling. In the second theoretical part, quantum mechanical methods have been used from an engineering perspective and have been evaluated with the respect to the applicability for solving practical problems. In the experimental part, ionic liquids and their physical and chemical properties as novel liquid materials have been focused. The combination of ionic liquids with inorganic porous support has been investigated. Furthermore, separations of different gases and vapours have been performed both with and without use of carriers.

Mass transport modelling

A simple mass transport model for facilitated transport through a liquid carrier membrane has been set up and implemented in finite elements software Femlab, which proved to be an excellent software for treatment of relatively simple engineering problems. The membrane phase has been considered to be made of an exemplary ionic liquid, for which its physical properties were estimated by published methods or were obtained by experiments. For maximum separation performance (i.e. maximum facilitation factor and hence maximum selectivity) the concentration based equilibrium constant concerning an exemplary carrier-permeant reaction has been calculated. For the purpose of thermodynamical evaluation, concentration based equilibrium constant has been converted to the „true“ thermodynamical equilibrium constant, whereupon the Gibbs free enthalpy change for the reaction of the carrier with the desired permeant was determined. It was found that Gibbs free enthalpy is in the range from $-12 \text{ kJ/mol}$ to $-18 \text{ kJ/mol}$. It can be concluded that the reaction takes place spontaneously and, since the contribution of reaction entropy change can generally be neglected in liquid phase, the Gibbs free enthalpy change can be also taken as reaction enthalpy.
Molecular Modelling

Techniques of molecular modelling in principle enable the calculation of almost all relevant engineering data without application of any measured parameters. This holds primarily for gas phase phenomena. However, treatment in condensed phase is also possible. Apart from the molecular structure, chemical reaction thermodynamics can be obtained by quantum mechanics, whereas the diffusion phenomena (diffusion coefficients) can be predicted by molecular dynamics.

Several known carriers (e.g. for oxygen and propylene) have been treated by common density functional theory methods. The treatment has been extended to not yet synthesised and investigated carriers. It was found that quantum mechanical methods, which are computationally „cheap” enough in order not to be prohibitive for the treatment of realistic problems, can currently not accurately predict the exact thermodynamical behavior of reversible carrier-permeant reactions. Furthermore, these methods are even not sensitive enough for in-silico optimisation of already existing carriers. In spite of the limited applicability and deficiencies of quantum mechanical methods, a few criteria could have been nevertheless stated, by which a potential carrier among proposed chemical structures may be identified. Firstly, the reaction of the carrier with the desired permeant typically does not show distinctive transition state barriers (activation energy is preferably less than 5 kJ/mol), which are in some cases completely missing (negative barriers, physisorption). Secondly, depending on the chosen DFT software and the options used, different reaction enthalpies and Gibbs free enthalpies for the same reaction are obtained ranging from $-50$ kJ/mol up to $-200$ kJ/mol. Favourable values of the reaction enthalpies for the potential carrier when using Turbomole software package lie between $-100$ kJ/mol and $-200$ kJ/mol, independent of whether the solvation effects were considered or not. Reaction enthalpies above $-100$ kJ/mol may lead to carriers whose optimum equilibrium constant is reached only at technically disadvantageous conditions, i.e. at very low temperatures. However, each reaction case must be considered separately.

The search for novel carriers via molecular modelling showed that in principle there are some compounds, which may be suitable for the fulfillment of the task of oxygen-nitrogen or propane-propylene separation. However, the costs factor for the synthesis of these compounds is expected to be immense and it is not likely that such compounds will find their way into industrial practice.

COSMOtherm, which is mainly used for the generation of accurate activity coefficients, is another molecular modelling tool that has been evaluated in this work. It was used for the prediction of Henry coefficients of different gases and vapours in ionic liquids. The obtained values do not exactly correspond with the experimental data, but general trends have physical meaning and can actually be well estimated. The main reason for the deviations lies in the missing or inappropriate internal parameterisation for some atoms constituting the ionic liquid, which is not accessible by the user. Nevertheless, COSMOtherm is the only tool that enables any reasonable prediction of thermo-physical data concerning ionic liquids. Its use can be recommended.

The estimation of diffusion coefficients has been performed in the case study by molecular dynamics using universal force field. So far, no appropriate force fields have been devel-
6.1. SUMMARY

oped for the treatment of systems consisting of particles with delocalized charges (systems like ionic liquids). The choice of the „correct” force field is crucial for obtaining realistic, i.e. physical meaningful results, but it is not the only limitation of practical usage of molecular dynamics, which in this work was found to be the computational resources. In the case study, diffusion coefficients obtained by molecular dynamics differ up to three orders of magnitude from the expected/measured values - they are far too high when compared to the diffusion coefficients derived from the permeation experiments. It has to be noted, however, that the common engineering estimation methods also fail to give reasonable results for diffusion coefficients in ionic liquids. It can be concluded that molecular dynamics methods require very long computational times and yield poor absolute values of diffusion coefficients. Furthermore, since their predictability character is modest too, they can not be used for the engineering daily routine yet. Diffusion coefficients are more efficiently, i.e. more accurately, determined experimentally.

Experiments on Novel Materials

In the experimental part of this work, some physical properties of ionic liquids that are crucial for their use as the liquid phase in liquid membranes have been determined. Apart from basic properties like density and viscosity, for the first time the permittivity constant, surface tension and wetting properties on different surfaces have been examined. Density of the most common ionic liquids ranges between 1300 and 1800 kg/m³. Absolute viscosities depend on the nature of the compound: the compounds used in this work display viscosity values around 30 mPa s at room temperature. In the technically relevant friction range ionic liquids behave as ideal Newtonian fluids. The relative permittivity of ionic liquids based on [BTA]⁻ anion lie between 8 and 18, for very polar sulfate based ionic liquids it is higher than 30. Surface tension of ionic liquids is slightly higher that that of common organic solvents. In this work, surface tension values between 30 and 40 mN/m were found. The wetting phenomena of ionic liquids on different inorganic supports could not be satisfactorily explained, but it seems that ionic liquids display strong intermolecular interactions, which in their nature can be compared to those of hydrogen bonding. The interactions with non-ionic matter are avoided and electrostatic interactions dominate. Surface tension and wetting influence the transmembrane pressures that can be applied to supported liquid membrane, i.e. to the liquid held in the pores of porous support by capillary forces. It was found experimentally that maximum transmembrane pressures amount to as high as 12 bar. The pressures that can be applied to ceramic support that potentially enable scale-up of the membrane separation unit are, however in the range of 3 to 4 bar.

Furthermore, the solubility of different gases and vapours has been investigated. In particular, the solubilities of propylene and propane as well as oxygen and nitrogen have been determined. It has been found that the solubility ratio of these vapours and gases behave no different than in other, more commonly used solvents. The solubility of propylene and oxygen is twice as high as that of propane and nitrogen, independent of the ionic liquid used. Nevertheless, the solubility of ionic liquids for vapours is generally higher than that of other solvents.
The solubility of gases and vapours in the membrane phase has shown a higher impact on the performance of the solution-diffusion liquid membranes than their diffusivity. Since the diffusion coefficients for propane and propylene as well as for oxygen and nitrogen are very similar, it was not surprising to find the experimental perm-selectivities and selectivities for these two separation problems around value of 2, which approximately correspond to the the ratio of the respective Henry's coefficients. The selectivity in membrane permeation experiments decreases with temperature, because the gas/vapour solubility decreases with increasing temperature. The absolute fluxes are with maximum values of about 40 dm³/m² h bar rather small. This is due to the considerable membrane thickness, which could not be reduced.

All attempts following the carrier approach in this thesis failed to give any satisfying results. The main reason is that classical carriers for propylene/propane separation (silver and cooper salts) have extremely low solubility in ionic liquids. A carrier for oxygen could be well dissolved in ionic liquid, however, it deactivated in the liquids phase, probably due to the carrier dimerisation or to strong coordination of the carrier’s active site.

6.2 Outlook

In order to provide a fully functional technical solution for separation of e.g. propylene from propylene/propane mixture or of oxygen form air by means of liquid carrier membranes, each individual field, which was the subject in this thesis, should be treated in more detail.

The mass transport model, which has been developed here and has provided a workable solution, should be extended to account for Stefan diffusion in the feed and the permeate phase. Furthermore, in order to circumvent the postulation of gas/vapour-liquid equilibrium at the membrane phase boundaries, an iterative procedure that could account for the mass transfer coefficients should be implemented.

In the field of molecular modelling other methods than DFT should be used. In particular, compound chemistries (e.g. G3MP2) that are specially designed for solving thermochemical problems should be applied. At present time, this is not possible, since these methods are not fully developed yet. Therefore, a considerable quantum chemical method development endeavour is required for the inclusion of all transition metals and preferably all elements of the periodic system in the compound chemistries. Molecular dynamics based on force fields should not be used. Instead, very promising and more universally valid Car-Parinello molecular dynamics, which is based on quantum mechanics, should be evaluated. I personally believe that the development of force fields, that can only be applied to selected problems (i.e. for treatment of ionic liquids) is a dead-end and a waste of time. Although CPMD might be even slower than classical MD, it should yield more realistic results.

In spite of the intensive research in the last decade, there is still insufficient knowledge available in the field of ionic liquids. Little is known on temperature dependence of gas and vapour solubilities, on miscibility with other liquids/solvents and solvation ability for solids. Parameters like thermal stability is also not known. The use of ionic liquids as
solvents for catalytical processes is in the early stage of development. Diffusion coefficients have also not been widely measured. Furthermore, none of the published correlations for estimation of physical and chemical data can be satisfactorily applied to ionic liquids.

For further improvement of liquid membranes based on ionic liquids three main topics remain and should be focused in the future. First topic is the development of task specific ionic liquids. Task specific ionic liquids include the aspect of catalytical activity. The second topic is the development of very thin and stable (porous) organic or inorganic supports. The third topic is thorough examination of the interactions between the ionic liquids and the supports.

6.3 German Summary (Zusammenfassung)

In der vorliegenden Arbeit wurde versucht, eine vollständige Entwicklung der flüssigen Membranen mit und ohne Chemoselektoren (Carriern) sowohl aus theoretischer als auch aus experimenteller Sicht anzugehen. Flüssige Membranen, deren aktive flüssige Phase aus Ionischen Flüssigkeiten besteht, sollen sowohl für Gas- als auch für Dampftrennungen eingesetzt werden.


6. SUMMARY AND OUTLOOK


Bei der Suche nach neuen Chemoselktoren (Carriern) durch die Anwendung der molekularen Modellierung hat sich herausgestellt, dass die nicht geeigneten Carrier sofort ausgeschlossen werden können. Darüberhinaus konnte gezeigt werden, dass es die geeigneten Carriermoléküle wenigstens im Prinzip geben kann. Allerdings ist die Synthese der vorgeschlagenen Verbindungen sowohl sehr kostenintensiv als auch sehr komplex, so dass man erwarten kann, auch in der Zukunft für Sauerstoff-Stickstoff und insbesondere für Propan-Propen Trennung keine industriell geeigneten Verbindungen finden und einsetzen zu können.

COSMOtherm, das hauptsächlich zur Berechnung von Aktivitätskoeffizienten eingesetzt wird, wurde in dieser Arbeit als weiteres Werkzeug der molekularen Modellierung evaluiert. Das Programm wurde für die Vorhersage der Henry Koeffizienten verschiedener Gase und


**Experimente mit neuen Materialien:** Im experimentellen Teil dieser Arbeit wurden einige physikalischen Eigenschaften der Ionischen Flüssigkeiten (ILs) bestimmt, die in der Herstellung flüssiger Membranen eine entscheidende Rolle spielen. Neben der Bestimmung der Dichte und Viskosität wurden zum ersten Mal die relativen Dielektrizitätskonstanten, Oberflächenspannungen und Benetzungseigenschaften verschiedener Ionischer Flüssigkeiten auf unterschiedlichen Substraten untersucht. Die Dichte der üblichen ILs liegt zwischen 1300 and 1800 kg/m$^3$. Absolute Viskositäten hängen stark von der Natur der Verbindung ab: die ILs, die in dieser Arbeit verwendet wurden, zeigen eine Viskosität um 30 mPa s bei Raumtemperatur. Im Bereich der technisch relevanten Scherraten verhalten sich Ionische Flüssigkeiten als Newtonsche Fluide. Die relative Dielektrizitätskonstante der [BTA]$^-$-basierten Ionischen Flüssigkeiten liegt zwischen 8 und 18, für sehr polare sulfatbasierte ILs liegen die Werte weit über 30. Die Oberflächenspannung der ILs ist etwas größer als die der üblichen organischen Lösungsmittel. In dieser Arbeit wurden Oberflächenspannungen zwischen 30 und 40 mN/m gefunden. Die Phänomene der Benetzung von verschiedenen anorganischen Trägern mit ILs konnten nicht zufriedenstellend erklärt werden, allerdings scheinen starke intermolekulare Wechselwirkungen, die mit Wasserstoffbrückenbindungen verglichen werden können, eine wesentliche Rolle zu spielen. Es wurde beobachtet, dass die Wechselwirkungen mit nicht-ionischer Materie von den ILs vermieden werden und dass die elektrostatischen Wechselwirkungen dominieren.
Die Oberflächenspannung und Benetzungseigenschaften beeinflussen die transmembrane Druckdifferenz, die an eine flüssige Membran (eine Flüssigkeit, die in Poren des porösen Trägers durch Kapillarkräfte gehalten wird) angelegt werden kann. Es wurde experimentell gefunden, dass die maximale transmembrane Druckdifferenz höchstens 12 bar beträgt. Die Drücke, die an eine scale-up fähige keramische Membran angelegt werden können, sind mit 3 bis 4 bar jedoch deutlich kleiner.


Alle Versuche in dieser Arbeit, um das Carrier-Konzept mit flüssigen Membranen zu verwirklichen, brachten keine zufriedenstellende Ergebnisse. Die Hauptursache dafür ist, dass die klassischen Carrier für Propen/Propan Trennung (Silber- und Kupfersalze) keine ausreichende Löslichkeit in Ionischen Flüssigkeiten besitzen. Der Chemoselektor für Sauerstoff konnte zwar gut in der Ionischen Flüssigkeit gelöst werden, wurde jedoch entweder durch die Dimerisierung des Carriers oder durch eine zu starke Koordination deaktiviert.
A Data assessment for mass transfer models

The Wilke-Chang or Perkins and Geankoplis techniques are suitable for the estimation of the diffusion coefficients. However, tabulated increments (e.g. for critical volume) are only available for common chemicals. The assessment of missing variables, in particular liquid molar volume, which is required for the usage of these techniques is shown in the following.

Liquid molar volume \( V_b \)

Experimental data on the liquid molar volume is only available for propylene and propane. Empirical methods must therefore be employed to obtain the values for the carriers and adducts used in this work (these are: Ni-dithiete, Ni-dithiete-propylene complex, copper-tetrachloroaluminate and its complex with propylene). A number of additive methods are presented in [116]. Each element and certain bond linkages are assigned numerical values, so that the molar volume at the normal boiling point can be calculated by addition of these values. Volume increments suggested by Le Bas have been proven to be reasonably accurate for a wide range of molecules. Table A.1 presents the suggested volume increments, which are correlated here to the appropriate van der Waals radii. The van der Waals radii have been obtained from molecular computations in Materials Studio and Spartan.

It is assumed that a proportional correlation exists between the volume increments and the respective van der Waals radius of each element. Plotting the given increment value over the respective van der Waals radius and fitting a line through the data points gives a formula which can be used to reasonably calculate volume increments of unknown elements if the respective van der Waals radius is given. This is illustrated in figure A.1:

The mathematical function of the line of best fit shown in figure A.1 obeys

\[
y = 1,3487x^{4.8428}
\]

where \( x \) refers to the van der Waals radius and \( y \) to the calculated volume increment. As an example, the volume increment of Ni can be determined to be 14.37 cm\(^3\)/mol.

It is important to note that not only the elements, but also certain bond linkages are considered when applying increment methods to estimate liquid molar volumes. It is suggested to deduct the values from the sum of the elements in case of a ring structure. For example, since Ni-dithiete includes two 5-membered ring structures, the value of 11.5 must be subtracted twice.
Table A.1: Liquid molar volume increments and *van der Waals* radii

<table>
<thead>
<tr>
<th>element name</th>
<th>volume increment [cm$^3$/mol]</th>
<th>vdW radius [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>14,8</td>
<td>1,7</td>
</tr>
<tr>
<td>H</td>
<td>3,7</td>
<td>1,2</td>
</tr>
<tr>
<td>O</td>
<td>7,4</td>
<td>1,52</td>
</tr>
<tr>
<td>N</td>
<td>12</td>
<td>1,55</td>
</tr>
<tr>
<td>Br</td>
<td>27</td>
<td>1,85</td>
</tr>
<tr>
<td>Cl</td>
<td>24,6</td>
<td>1,75</td>
</tr>
<tr>
<td>F</td>
<td>8,7</td>
<td>1,47</td>
</tr>
<tr>
<td>I</td>
<td>37</td>
<td>1,98</td>
</tr>
<tr>
<td>S</td>
<td>25,6</td>
<td>1,8</td>
</tr>
<tr>
<td>Al</td>
<td>N/A</td>
<td>1,43</td>
</tr>
<tr>
<td>Ni</td>
<td>N/A</td>
<td>1,63</td>
</tr>
<tr>
<td>Cu</td>
<td>N/A</td>
<td>1,4</td>
</tr>
</tbody>
</table>

Figure A.1: *Van der Waals* radii and liquid molar volume increments
Table A.2 illustrates the summation of the increments for Ni-dithiete, propane and propylene:

Table A.2: Summation of liquid molar volume increments

<table>
<thead>
<tr>
<th>Increment [cm³/mol]</th>
<th>Increment [cm³/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>propylene</td>
<td>Ni-dithiete</td>
</tr>
<tr>
<td>C</td>
<td>14,8</td>
</tr>
<tr>
<td>C</td>
<td>14,8</td>
</tr>
<tr>
<td>C</td>
<td>14,8</td>
</tr>
<tr>
<td>H</td>
<td>3,7</td>
</tr>
<tr>
<td>H</td>
<td>3,7</td>
</tr>
<tr>
<td>H</td>
<td>3,7</td>
</tr>
<tr>
<td>H</td>
<td>3,7</td>
</tr>
<tr>
<td>H</td>
<td>3,7</td>
</tr>
<tr>
<td>∑</td>
<td>66,6</td>
</tr>
<tr>
<td>propane</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>14,8</td>
</tr>
<tr>
<td>C</td>
<td>14,8</td>
</tr>
<tr>
<td>C</td>
<td>14,8</td>
</tr>
<tr>
<td>H</td>
<td>3,7</td>
</tr>
<tr>
<td>H</td>
<td>3,7</td>
</tr>
<tr>
<td>H</td>
<td>3,7</td>
</tr>
<tr>
<td>H</td>
<td>3,7</td>
</tr>
<tr>
<td>H</td>
<td>3,7</td>
</tr>
<tr>
<td>H</td>
<td>3,7</td>
</tr>
<tr>
<td>∑</td>
<td>74</td>
</tr>
<tr>
<td>Ni-Complex</td>
<td></td>
</tr>
<tr>
<td>Ni-dithiete</td>
<td>316,57</td>
</tr>
<tr>
<td>propylene</td>
<td>66,6</td>
</tr>
<tr>
<td>∑</td>
<td>383,17</td>
</tr>
<tr>
<td>∑</td>
<td>316,57</td>
</tr>
</tbody>
</table>

Note on association factor $\phi_j$

The association factor $\phi$ accounts for hydrogen bonding or electrostatic interactions in the solvent. Wilke and Chang recommend that $\phi$ be chosen as 2.6 if the solvent is water, 1.9 if it is methanol, and 1.0 if the molecules are not aggregated. I assume that there is a correlation between association factor and surface tension, which is used here,
or to relative permittivity. According to the surface tension of water and methanol, the association factor for the ionic liquid can be set to 2.2. The interactions of other components (propylene, propane, carrier) are considered to be negligible.
B Additional information on molecular modelling

In order to be able to use molecular modelling and in particular quantum mechanical methods as a tool in chemical engineering, it is essential to understand the basics of how the calculations are set up, how they are conducted, what can be calculated, and where to locate the expected results. Whereas for the most or at least for many problems concerning chemical reactions there exists a routine procedure, intuition is especially needed in determining transition states.

B.1 Physical quantities in molecular modelling

Chemical engineer is usually interested in the reaction enthalpies and the reaction free energies or in general energetics within the so called reaction coordinate, which enables e.g. the calculation of the reaction equilibrium. Target physical quantities of interest are listed in Table B.1. The interpretation of these quantities is partly accomplished according to the Gaussian program output [299] and is the subject of these appendix.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_0$</td>
<td>electronic energy</td>
</tr>
<tr>
<td>$\varepsilon_{ZPVE}$</td>
<td>zero point vibrational energy</td>
</tr>
<tr>
<td>$E_{tot}$</td>
<td>thermal correction to energy</td>
</tr>
<tr>
<td>$E_{int}$</td>
<td>internal energy</td>
</tr>
<tr>
<td>$H_{corr}$</td>
<td>thermal correction to enthalpy</td>
</tr>
<tr>
<td>$G_{corr}$</td>
<td>thermal correction to Gibbs free energy</td>
</tr>
</tbody>
</table>

In the following subsections one can find a short and comprehensible “how to” introduction, which is meant to cover all procedures used in this thesis and which should enable even a novice to understand and reconstruct the results. However, I will annotate the situations where problems usually arise and where one should take a specialists’ advice.

B.1.1 Quantum mechanical methods

*Ab-initio calculations* are strictly based on the theoretical principles and do not include any experimental data. The energy expression in *ab-initio* methods is derived from
Schrödinger equation

\[ H\psi = E\psi, \]

where \( H \) is the Hamiltonian (operator of kinetic and potential energy), \( \psi \) the wave function and \( E \) represents the energy eigenvalues to the given wavefunction \((\varepsilon_0, \varepsilon_1, \varepsilon_2 \ldots \varepsilon_n)\) of the system. As default, Born-Oppenheimer approximation is assumed [231], i.e. Hamiltonian expression for the potential and the kinetic energy include all the electrons and stationary atomic nuclei. Given the basis sets (atomic orbitals) of all atoms included in a molecule, a set of molecular orbitals is obtained by linear combination of atomic orbitals approximation (LCAO). Molecular orbital coefficients are calculated in an iterative routine called self consistent field calculation (SCF). In the solution of so called Roothaan-Hall equations, wavefunctions (eigenfunctions) is obtained, whereupon the eigenvalues (energies) of system are calculated, yielding in \((\varepsilon_0)\) for the electronic ground state. In the course of the search for the geometry of the optimised molecule structure, several optimizing algorithms exist, among which the steepest descent routine is the most popular. In the minimisation procedure atoms coordinates are moved in such way that final structure yields a minimum energy from Schrödinger equation.

 Basically, two methods are important for engineering purposes: Hartree-Fock (HF) and Møler-Plesset second order perturbation theory (MP2). Correlated methods like higher order Møler-Plesset perturbation theory (MPn), multi-configurational self-consistent field (MCSCF), configuration interaction (CI), coupled cluster theory (CC), where electron-electron interactions are taken into account, are computationally too expensive to be performed for real (industrial) problems and could also not be used for all problems within this thesis.

In density functional theory (DFT), the basic principles of calculations are the same as in HF method, but the energy expression is based on electron density rather than on wave function. Initial electron density is derived from LCAO ansatz.

The accuracy performance of DFT methods, when compared to experimental results, can not be systematically improved as in case of correlated ab-initio methods. The results on reaction enthalpies and reaction free energies may be poor to fairly good. Since there is no way to improve the accuracy, even with the usage of larger basis sets (i.e. more accurate description of atom orbitals), results have to be taken as they are. Furthermore, since they can not be explicitly checked for correctness, they must be met with caution. It is sometimes reasonable to test e.g LDA (local density approximation) against GGA (gradient approximation, e.g. BLYP) methods and check, whether the results are consistent. For transition metals, using hybrid functionals that include HF corrections, like B3LYP, is highly recommended. This may be the most reasonable approach, since other quantum mechanical models will be often computationally prohibitive. LDA method with functional BP (Becke-Pardow) satisfies most of chemistry. However, in general, GGA produces better results.

In order to be sure that geometries obtained from DFT calculations are reasonable, they should always be compared to either experimental data (x-ray diffraction, spectroscopy data), if available or inspected by another quantum chemical method (e.g. HF, MP2). If calculations using HF methods fail, the MP2 will also lead to nonsense results.
Basic mathematical energy expressions that underlie the above methods (HF, MP, CC, DFT etc.) and yield $\varepsilon_0$ can be found in [300]. An engineer should usually not be concerned about their implementation in the particular software: this is the subject of the development of methods within theoretical chemistry.

**Basis sets**

Depending on software used, five types of basis sets are implemented: Gaussian Type Orbital (GTO), Pople basis sets, Slater Type Orbital (STO), Numerical Orbitals (NO) and plane wave basis sets. The later are used in solid state physics and recently also in CPMD (Carr-Parinello Molecular Dynamics). Pople basis sets (e.g. 3-21G) are most widely used. In order to increase the accuracy, polarization functions are added (* or (d), ** or (d,p)). For anions, diffuse functions (+, ++) must be used. The largest basis set used in this thesis is 6-311+G(2p,2d). For transition metals, it is reasonable not to include all electrons into the calculation. Instead, effective core potentials (ECP) or pseudopotentials can be used. As with the abundance of basis sets (cp. [301]), there are also several ECPs available. As a user, one has to have confidence that ECPs are properly chosen by default in given software and relativistic effects are included [302]. For transition metals, LANL2DZ [184] ECPs are recommended.

**Model chemistries**

Model chemistries [303] like G2 [304, 305], G3 [306] or G3(MP2) [307] are empirically developed theoretical constructs that extrapolate values of different computationally affordable methods (HF, MP2, CCSD(T) etc) using different basis sets towards the true solution for energy of Schrödinger equation accounting for enthalpies of formation. For engineering problems they are usually computationally still too expensive and they do not deliver results covering temperature dependant thermochemistry.

**Special features**

*Electron smearing* may be used to overcome occasional convergence difficulties for the SCF procedure. It is implemented in Turbomole, DMol³ and ADF. The idea is to distribute electron occupations fractionally over a few states around the Fermi level by a pseudo-thermal distribution function [308]. The applied distribution of occupations is not an approximation to the finite-temperature case and has no physical meaning. The smearing „trick“ is only to be used to overcome convergence difficulties - one should not use the results as a meaningful outcome. Having reached convergence with it, one should typically do a follow-up restart calculation without smearing, using the converged outcomes to hopefully get the thing to converge properly. A typical „allowed“ application is the usage of smearing during geometry optimizations, because the intermediate geometries are not relevant anyway and only a step towards the final results. Smear parameter may be reasonably varied between 0,001 and 0,1 Hartree, default being 0,01 or 0,05 Hartree depending on software. Alternatively, temperature window for pseudo-thermal distribution
may be specified. For usage details see [309] and [310]. Contributions of electronic interaction energy in DFT are expressed as functionals of the electronic density. These functionals include exchange correlation term and the Coulomb potential term. Resolution of identity (RI) is an approximation for the calculation of Coulomb potential contribution, where the density is represented by an auxiliary basis set [311]. RI is implemented in Turbomole program, making it extremely fast [312].

B.1.2 Accounting for solvation effects

Most of the chemistry today is conducted in condensed, usually liquid phase. In the gas phase it is assumed that a molecule does not interact with neighboring molecules and can be considered to be isolated. If solvation problems are to be tackled, three possible approaches can be used. One can treat a molecular cluster in vacuum, which would make an ensemble of the molecule of interest together with the solvent molecules being in the immediate vicinity surrounding it. In this case, one encounters errors due to the boundary effects. This effects can be diminished by the usage of so called periodic boundary conditions (PBC). Here, a molecule of interest is put in a box, which is afterwards filled with solvent molecules. Some programs (e.g. Amorphous Cell with MS Modelling) allow the user to specify either the desired final density of the system or the number of solvent molecules to be randomly put in the box (e.g. Hyperchem). The size of the box must be chosen in such a way that the images of the solute molecule are sufficiently far away from each other forming “ideally” diluted solution. Both explicit solvent techniques require great amount of computational resources due to numerous atoms (and thus basis functions) involved. Today, convenient and more accurate work-around methods are available for determination of wave function of solute molecule in the solvent molecules without the computation of the wave function for the ensemble. In these models, solute molecule occupies a cavity within a uniform medium that represents the solvent environment. Solvent molecules are replaced by a continuum that is specified by its relative dielectric constant $\epsilon_r$. The umbrella term for these models is continuous solvation models (CSM). Whereas in explicit solvent methods the net effect of interactions (e.g. dipole-dipole) that the solute experiences by interacting with neighboring molecules is called reaction field, this reaction field becomes a potential term that has to be added to the Hamiltonian of solute [313]. Since this potential depends on the dipole moment of the solute, and dipole moment depends on its wave function, the consistency between the interaction field and the wave function must be reached in an iterative procedure similar to that of the calculation of coefficients in molecular orbitals from basis sets of atoms. Quantum mechanical models for solutions are called self-consistent-reaction field (SCRF). Several SCRF models have been devised [314], which primarily differ in the shape of the cavity occupied by the solute. In Onsager SCRF method for instance, one has to specify the spherical cavity with radius of the solute. The radius of the sphere can be calculated from a volume of the molecule that is defined by a electron probability density (in electrons per Bohr$^3$)\(^1\). Recommended value in Onsager model is 0.001 $\epsilon$ \text{Bohr}$. In polarizable

\(^1\)The electron probability density surface of 0.002 $\epsilon$ \text{Bohr} corresponds more or less to van der Waals interaction distance. Dependant on the software used, molecular volumes could not be reproduced in
B.1. PHYSICAL QUANTITIES IN MOLECULAR MODELLING

continuum model (PCM) more realistic cavity shape is used. It is formed of overlapping spheres centered on the atomic nuclei, where each of these spheres is taken 1.2 times the van der Waals radius of the corresponding atom\(^2\). Isodensity PCM (IPCM) method uses a “real” cavity defined by the molecules surface of \(0.0004 \text{ Å}^3\). Self-consistent isodensity PCM method refines the cavity shape to be consistent with the wave function. All solvent models implemented so far do not include any reasonable thermochemistry. Therefore, among engineers, COSMO (Conductor-like Screening Model) method in connection with software package COSMOtherm [114] became popular due to its robustness and efficiency. COSMO is a deviation of PCM, where the solvents permittivity is set to infinity \(\varepsilon_r = \infty\). Although some quantum chemical programs allow values of relative permittivity smaller 1, these results have no physical meaning. Test calculations have shown that the energy of non-charged polar solute molecules significantly change only within \(1 < \varepsilon_r < 80\). For \(80 < \varepsilon_r < \infty\), the energy changes usually lie below \(3 \cdot 10^{-4}\) Hartree (< 1 kJ/mol).

B.1.3 Vibrational analysis

In the pursuing the thermochemistry, the next step after finding minimum on PES, that is the value of \(\varepsilon_0\), procedure called vibrational analysis is performed. It leads firstly to \(\varepsilon_{ZPVE}\). Zero point vibrational energy is the vibrational energy of the molecule that is present even at 0 K. It is temperature independent:

\[
\varepsilon_{ZPVE} = R \sum_i \frac{h_P}{2k_B} \omega_i,
\]

Here, \(h_P\) is Planck’s constant, \(k_B\) Boltzman’s constant and \(\omega_i\) the individual frequency mode of the molecule. Note that frequencies \(v_i\) are usually given in unit 1/cm and must be converted to \(\omega_i\) with unit 1/s by simple multiplication with the speed of light \(c\).

Vibrational analysis, a step towards molecule’s properties, can be done analytically or numerically. The calculation is in both cases extremely time consuming. Analytical calculations, that include the first and second derivation of energy to geometry function, are faster but usually cannot be restarted if calculation did not run to the end. In numerical calculation, one can imagine that all atoms of the molecule are subsequently moved from their equilibrium positions in three (or six) directions \((x, y, z)\) by certain small distance \((\Delta x, \Delta y, \Delta z)\) or \((-\Delta x, -\Delta y, -\Delta z, \text{respectively})\). Single point calculation, i.e. calculation where no coordinates are moved, is conducted at each distorted geometry, leading to the energy and the gradient and necessarily to the second derivative, called Hessian matrix. In this procedure, potential energy surface in minimum can only be approximated by harmonic oscillator (quadratic potential function).

Vibrations in ab-initio calculations and density functional theory must be scaled by empirical correction factor [316]. This is performed in order to fit the calculated data to several comparison tests even for the same electron density. However, the effect of radius and therefore cavity extension seems to be relatively small.

\(^2\)This resembles much the maximum (exposed) solvent accessible surface area (SASA), which is used in molecular modelling of proteins, especially for calculation of solvation energy, hydration effects, drug binding and molecular docking [315].
B. ADDITIONAL INFORMATION ON MOLECULAR MODELLING

Experimentally obtained spectroscopic data (e.g. IR spectra). Calculated vibrational frequencies in HF and DFT are usually too high and will be scaled by 0.9 by default. This holds for both zero point and thermal vibrations contribution. The access to scaling factor input is enabled by Gaussian utility program freqcheck and freed in Turbomole. The respective outputs from freq and aoforce routes give the results without scaling. In “pure” DFT programs like DMol3 and ADF the scaling is performed automatically.

B.1.4 Thermal contributions to energy

Thermal contributions, in particular those to internal thermal energy and entropy, are derived from differentiation of translational, rotational, vibrational and electronic partition function of the given molecule with respect to the temperature. Partition functions themselves can be derived from quantum mechanical models for (discrete) eigenvalues $\epsilon_i$ of the respective energy contribution [118, 317]. General formulation of an arbitrary partition function for an isolated molecule is given by

$$q = \sum_i g_i e^{\frac{\epsilon_i}{k_B T}},$$

where $g_i$ is the degeneracy level of the $\epsilon_i$-th energy state.

Partition functions of interest can be formulated in the following manner:

**Translation:**

$$q_t = \left(\frac{2\pi mk_B T}{h^2}\right)^\frac{3}{2} V$$

where $V$ is volume per molecule of ideal gas according to:

$$V = \frac{k_B T}{p}.$$  

In this case, partition function is without unit (and values for the translational partition function can be found in this form the Gaussian or Turbomole output files). However, as we will soon see, it is sometimes useful to apply the equation

$$q_t = \left(\frac{2\pi mk_B T}{h^2}\right)^\frac{3}{2},$$

which has a unit [1/m$^3$]. Moreover, $V$ can also be useful expressed in volume of 1 mol of ideal gas. Then $q_t$ has the unit [1/mol m$^3$].

---

3The scaling factor is still the subject of controversial discussions, cp. www.ccl.net. Probably the best way to obtain a scaling factor, which is certainly better than a generic scaling factor for a particular level of theory, is to perform another ab-initio calculation at the same level of theory on an analogous molecule for which the vibrational frequencies are known. One can then apply the scaling factor which best suits the known molecule to the molecule in question.

4Partition function is a quantity that describes the extent of the achievable states of the thermodynamical system. Partition function is the counterpart of wavefunction on macrosopic level.
Rotation:

\[ q_{\text{rot}} = \begin{cases} 1 & \text{for atoms,} \\ \left(\frac{8\pi^2 k_B T}{\sigma h_p}\right) \frac{I}{\sigma} & \text{for linear molecules,} \\ \left(\frac{8\pi^2 k_B T}{\sigma h_p}\right) \frac{3}{2} \frac{\sqrt{\pi} I_A I_B I_C}{\sigma} & \text{for non-linear molecules.} \end{cases} \]

\( I \), \( I_A \), \( I_B \) and \( I_C \) are the principal moments of inertia, \( \sigma \) is a symmetry number [318].

Vibration: In case of vibration, there are two possibilities to define the “zero reference point”. Zero reference can be taken to be the bottom of the internuclear potential well (BOT) as shown here, or the first vibrational level, i.e. zero of molecular energy. For detailed discussion, see [143].

\[ q_{\text{vib}} = \prod_i \frac{e^{-\hbar \omega_i} - 1}{e^{-\hbar \omega_i} + 1} \]

Electronic: As simplification, molecules treated in engineering tasks will always be considered to find themselves in their electronic ground state. The energy of ground state \( \epsilon_0 \) is then simply set to zero. Therefore

\[ q_{\text{elect}} = s_0 e^{\frac{\epsilon_0}{k_B T}} = s_0 \]

where \( s_0 \) is the degeneracy of the energy ground level, here being the electronic spin of the molecule. With few exceptions (also encountered in the thesis), molecular spin is 1, i.e. all electrons are paired \( s_0=1 \). Doublets and triplets yield \( s_0=2 \) and \( s_0=3 \), respectively.

The total internal thermal energy is given by the following sum:

\[ E_{\text{tot}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elect}} \]

the total entropy by:

\[ S_{\text{tot}} = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{elect}} \]

Reasonable entropy values can be computed only on single, isolated molecules. Entropy calculations based on the first principles are, when applied to molecular ensembles, very poorly defined. Phenomena connected with unusual entropical effects (e.g. stabilisation of hydrophobic proteins in aqueous environment) must still be approached experimentally [319, 320, 321].

The results of individual contributions to internal thermal energy are:

Translational thermal energy:

\[ E_{\text{trans}} = \frac{3}{2} RT \]

Rotational thermal energy:

\[ E_{\text{rot}} = \begin{cases} 0 & \text{for atoms} \\ RT & \text{for linear molecules} \\ \frac{3}{2} RT & \text{for non-linear molecules} \end{cases} \]
Vibrational thermal energy: Already having performed the vibrational analysis, now all the information is available for the calculation of the vibrational thermal energy for finite temperature:

\[ E_{\text{vib}} = R \sum_i \frac{\hbar P}{2k_B} \omega_i + R \sum_i \frac{\hbar P}{k_B} \omega_i e^{\frac{\hbar P}{k_B} \omega_i} - 1, \]

the first term being zero point vibrational frequency - which, of course, must not be accounted for twice.

Electronic thermal energy:

\[ E_{\text{elect}} = 0. \]

In thermochemistry, entropy \( S \) is an important quantity, connecting free Gibbs energy with enthalpy according to:

\[ G = H - T \cdot S \]

Individual contributions to entropy must be formulated through the corresponding partition function:

**Translational entropy:**

\[ S_{\text{trans}} = R \left( \ln(q_{\text{trans}} + \frac{5}{2}) \right) \]

**Rotational entropy:**

\[ S_{\text{rot}} = \begin{cases} 0 & \text{for atoms} \\ R(\ln q_{\text{rot}} + 1) & \text{for linear molecules} \\ R(\ln q_{\text{rot}} + \frac{3}{2}) & \text{for non-linear molecules} \end{cases} \]

**Vibrational entropy:**

\[ S_{\text{vib}} = R \sum_i \left( \frac{\hbar P}{k_B T} \omega_i - \ln(1 - e^{\frac{\hbar P}{k_B T} \omega_i}) \right). \]

the first term being zero point vibrational frequency - which, of course, must not be accounted for twice. For discussion, where to take zero reference point - be it the bottom of the well or the first vibrational level.

**Electronic entropy:**

\[ S_{\text{elect}} = R \ln s \]

Above, I have stated total internal thermal energy \( E_{\text{tot}} \). In several textbooks, one also finds another term called internal energy:

\[ E_{\text{int}} = \varepsilon_0 + \varepsilon_{ZPVE} + E_{\text{tot}}. \]
B.2. TRANSITION STATES

The sum $\varepsilon_0 + \varepsilon_{ZPVE}$ refers to absolute zero. $E_{tot}$ refers to thermal correction $E_{tot}$ above the defined absolute zero, i.e. it does not include zero point energy. This additional term seems to be superfluous at first, however, one can write down the total enthalpy of the molecule as:

$$H_{tot} = E_{int} + RT,$$

where in the relation of the internal energy $E_{int}$ to the total enthalpy function expansion work of 1 mol of ideal gas must be accounted for $pV = RT$.

Considering the thermal correction to enthalpy $H_{corr}$ only (applying correct units for $E_{tot}$, i.e. hartree or J/mol, respectively):

$$H_{corr} = E_{tot} + k_B T \cdot \text{per mol} = E_{tot} + RT$$

From partition functions, molecular entropy is known and correction to Gibbs free energy $G_{corr}$ can be calculated by:

$$G_{corr} = H_{corr} - T S_{tot}.$$  

Sometimes, one can also find these additional relationships useful, namely:

$$\mu = \varepsilon_{ZPVE} - RT \cdot \ln(q_{trans}q_{rot}q_{vib}) \quad \text{and} \quad S_{tot} = \frac{E_{tot} + RT - \mu}{T},$$

where $\mu$ is the chemical potential and $E_{tot}$ does include zero point correction.

Now, we have all required quantities to cover the thermochemistry and can turn to kinetics.

B.2 Transition states

Obtaining the correct transition states (TS) is perhaps the trickiest issue in the whole quantum mechanics. In order to find the molecular geometry that corresponds to a postulated transition state between reactants and products, which can not be experimentally proven or observed, some strategic approaches are known. The methods for locating TS fall into two categories: those using only local information and methods that interpolate between the two minima, alternatively also using approximate TS.

B.2.1 Getting transition states

The easiest way exists for known reactions (e.g Diels-Alders), where several programs use database supported methods to produce a good initial guesses for the geometry [322]. For producing initial guesses, single point calculations can be performed accompanied by partial freezing of atomic coordinates or by usage of dynamic constraints. From here on,
local information (gradient, Hessian matrix) is used: methods are called gradient norm minimization (local or conjugate gradient) and Newton-Raphson method, respectively. The later is also called “eigenvector following” method. Although computationally very expensive, it be considered a working horse of TS optimisation techniques, where transition state is calculated by following the vibration mode that corresponds to the chosen imaginary frequency. Even in such a case, however, successful location of transition state is not guaranteed. Actually, nothing is guaranteed to work in TS search!

LST (linear synchronous transit), QST (quadratic synchronous transit), „saddle” optimization and chain method try to use reactant and product information to determine the TS. LST method forms the geometry difference vector between the reactant and product. Then it locates the highest energy structure along this line. The assumption is that all variables change at the same rate along the reaction path, which is not true. In QST the reaction path is approximated by a parabola instead of a straight line. This parabola is determined by locating the maximum on the LST path and then minimizing the energy in directions perpendicular to the LST path. The QST path is then searched for an energy maximum.

In the saddle algorithm, the lower of the two energy minima is identified and taken for a trial geometry calculation by displacing the geometry a fraction towards the higher energy minimum. The trial structure is optimized with the constraint that the distance to the highest energy minimum is held constant. The new endpoint is compared with the other endpoint. The two geometries will gradually converge based on a low energy structure intermediate between the original two minima.

The chain method calculates the energy at a series of points placed at regular intervals along a suitable reaction coordinate. The highest energy point on this path is allowed to relax by appropriate step size along a direction defined by the gradient component orthogonal to the line between the two neighboring points. This process is repeated with the new highest energy point until the gradient becomes tangential to the path. The current highest energy point cannot be further relaxed and is instead moved to a maximum along the path.

B.2.2 About spin in transition states

One important step in setting up a calculation for the search of the transition state molecular structure is not only to provide reasonable starting geometry of the molecules involved but to make allowance for spin angular momentum. Spin multiplicity gives the number of possible orientations, calculated as $2S + 1$, of the spin angular momentum corresponding to a given total spin quantum number ($S$), for the same spatial electronic wavefunction [323]. In computational chemistry, spin angular momentum $S$ is contributed by unpaired electrons. In systems where all electrons are paired, $S = 0$ and multiplicity is then $2 \cdot 0 + 1 = 1$ which corresponds to a singlet state. Each unpaired electron adds a spin angular momentum of $S = \frac{1}{2}$ to the molecule. Therefore, if molecule has one unpaired electron, it will be a doublet $2 \cdot \frac{1}{2} + 1 = 2$, a molecule with two, three, four, five unpaired electrons a triplet $S = 1$, quadruplet $S = \frac{3}{2}$, quintet $S = 2$, sextet $S = \frac{5}{2}$, respectively.
B.2. TRANSITION STATES

Now, what is the spin state of transition state if particles of different spin states react with each other? In this case, Clebsch-Gordan rules have to be applied. Here, only simple answer from not so straightforward theory [324] is given. Let be given molecules $M_1$ and $M_2$ having spin states $s_1$ and $s_2$. The possible spins of the potential transition state can be, $i$ being positive integer, calculated with:

$$s_{TS} = |s_1 + s_2| \quad \cdots \quad |(s_1 + s_2) - i| \quad \cdots \quad |s_1 - s_2|$$

**Examples:** In case of doublet ground state of one reactant (e.g. Co-salene) and triplet ground state of the second reactant (e.g. oxygen), two possibilities exist for the transition state spin angular momentum: it can either be a doublet or a quartet. Two triplets can combine to quintet, triplet or singlet. Generally, geometry optimization of transition state structure should be performed at all possible spin states, making the computation very expensive by all the combinatorial options. After all calculations, transition state with the lowest energy should be retained, others discarded.

B.2.3 Transition state confirmation

Local energy maximum on PSE is characterised by one negative eigenvalue in Hessian matrix, leading to one single „imaginary frequency“. One should visualize this negative eigenvalue, i.e. examine the mode of imaginary frequency and check, if it corresponds to the proper bond breaking. If it does, it is further reasonable to perform intrinsic reaction path (IRP) calculation in order to show that the transition state relaxes to form the products and can be reached on potential energy surface from the reactants. If it is found that reactants and products are not connected directly, another transition state must be searched for.

Reaction path calculation is started at a saddle point and takes successive steps in the direction of the negative gradient. This steepest descent approach leads to a minimum energy path (MEP)\(^5\). If the coordinate system is mass-weighted, this is called an intrinsic reaction coordinate (IRC). IRC calculation requires force constants at least in the very first step. Optional, force constants can be calculated in every IRC step.

A recently developed minimum energy path calculations uses the nudged elastic band (NEB) method that introduces a fictitious spring force between the neighboring points on the path [325]. This ensures continuity of the path and projection of the force so that the system converges to the MEP. The NEB method has been used widely in solid-state physics and has recently been applied to molecules as well but is not widely implemented in software packages. NEB is fast, but only qualitative alternative to IRC.

Searching for transition state in solvents is especially difficult, because the computation requires a “closed cavity surface”, i.e. reactants and products must be so close to each other that they can be described by one single cavity. This is often not the case (e.g. in proton

---

\(^5\) MEP is the path that would be produced by a molecular dynamics (MD) simulation starting at the TS using completely damped velocities and infinitesimal steps. Each point on the IRP is an energy minimum in all directions except one, which defines the direction of the IRP. This pathway also corresponds to the intuitive MEP connecting two structures.
transfer reactions, where tunniling might play an important role) and the calculations fail to converge.

Theoretically, having energies of reactants/products and transition state and their partition functions, it is possible to get some information on kinetics of the reaction by applying transition state theory.

**B.3 Examination of reaction energetics and kinetics**

**Enthalpy and free energy of formation**

Let the molecule M be composed of i atoms. Each individual sort of atom A, being present in the molecule for a times, contributes its heat of formation $\Delta_f H^o(A, 0K)$ and its electronic energy $\varepsilon(A)$ to the energy of the molecule. The enthalpy of formation for the molecule at 0 K is given by:

$$\Delta_f H^o(M, 0K) = \sum_i a \Delta_f H^o(A, 0K) - D_0(M),$$

where $D_0(M)$ is the atomization energy of the respective molecule:

$$D_0(M) = \sum_i a \varepsilon(A) - (\varepsilon_0(M) - \varepsilon_{ZPE}(M)).$$

Heats of formation for atoms $\Delta_f H^o(A)$, the enthalpy corrections $H^o_A(T) - H^o_A(0K)$ for several temperatures T and entropies for the atomic elements $S^o(A)$ are tabulated [326]. With this data, those at 298,15 K being of special interest, one can calculate the desired heat of formation for the molecule M:

$$\Delta_f H^o(M, 298, 15K) = \Delta_f H^o(M, 0K) + (H^o_M(298, 15K) - H^o_M(0K)) - \sum_i a(\Delta_f H^o_A(298, 15K) - H^o_A(0K)).$$

For calculation for Gibbs free energy of formation, entropy term must be added:

$$\Delta_f G^o(M, 298, 15K) = \Delta_f H^o(M, 298, 15K) - 298,15 (S^o(M, 298, 15K) - \sum_i a(S^o_A(298, 15K)).$$

Quantum mechanic models used for engineering purposes (HF, MP2, DFT) are not accurate enough for calculation of enthalpies and free energies of formation. Absolute values they can provide are far away from being reasonable. In this case, one has to use highly correlated models (e.g. CCSD(T)). However, even these do not guarantee proper correlation to measured values.
B.3. EXAMINATION OF REACTION ENERGETICS AND KINETICS

Reaction enthalpies and reaction free energies

Since the errors of non-correlated HF, MP2 and especially DFT methods can be considered to be systematic, they can be used - in contrast to enthalpies of formation - for evaluation of the relative energetics of certain reaction. For this purpose, it is reasonable to have the following sums ready for further calculation:

\(-\varepsilon_0 + \varepsilon_{ZPVE}\)

\(-\varepsilon_0 + E_{tot}\)

\(-\varepsilon_0 + H_{corr}\)

\(-\varepsilon_0 + G_{corr}\)

They are provided in output of Gaussian program, but more correctly they should be extracted from freqcheck output for each temperature of interest separately. For other programs, I have prepared utilities that convert results according to Gaussian scheme. In these cases, \(G_{corr,M}\) must explicitly be calculated from entropy and enthalpy.

The numbers in the last two rows can be directly plugged into the following equations:

\[\Delta H_r = \sum_M m(\varepsilon_{0,M} + H_{corr,M})\]

\[\Delta G_r = \sum_M m(\varepsilon_{0,M} + G_{corr,M})\]

where \(M\) refers to each of the molecules involved in reaction. Stoichiometry is accounted for by stoichiometric coefficient \(m\) (which are negative for the reactants and positive for products). Again, \(H_{corr,M}\) and \(G_{corr,M}\) already include zero point vibrational energy. Exactly the same applies for the reaction energetics in solution.

Chemical equilibrium

There are two ways in obtaining the two kinds of equilibrium constant for the ideal reaction:

\[A + B \rightleftharpoons C.\]

One can directly apply the equation:

\[K_a(T) = e^{-\frac{\Delta G(T)}{RT}},\]

where \(K_a\), the thermodynamic equilibrium constant. This \(K_a\) relates to fugacities or to activity coefficients and mol fractions, respectively. If \(K_a\) is greater than 1, the reaction
will be spontaneous, otherwise not. Since activity coefficients are usually known for real systems, one can not relate $K_a$ to real mol fractions.

On the other hand, one can use the equation that includes partition functions of the respective species in the following manner:

$$K_p(T) = (k_B T)^{-1} \frac{q_{tot,C}}{q_{tot,A}q_{tot,B}} = (k_B T)^{-1} K_c(T),$$

where $q_{tot,i}$ is composed of individual contributions of partition functions as given above. In our case, the unit of $K_p$ is 1/Pa, when we use 1/m$^3$ as the unit for translational partition function. If one would like to obtain $K_c$ in order to compare it to experimental values, if is practical to express the translational partition function in units 1/(mol m$^3$).

The complete derivation of equilibrium constants from canonical ensemble in terms of partition functions is best presented in [143], where also many practical examples are given.

Note that $K_a$ and $K_p$ can hardly be related to each other [141]: whereas $K_a$ is and must be dimensionless, $K_p$ or $K_c$ usually do have some units depending on stoichiometry of the reaction. Therefore, the values of all these quantities can not be the same\(^6\).

**Strict application of transition state theory**

Transition state theory (TST) is used to calculate the rates of gas phase reactions. It is based on Eyring’s considerations building on the Arrhenius model. We consider the following bimolecular example reaction (which I have used for the purpose of carrier reaction evaluation in the thesis):

$$A + B \rightleftharpoons [A-B]^\dagger \rightarrow C,$$

where A-B$^3$ is the (geometry of the) postulated transition state. The corresponding rate of reaction can be written as:

$$k = \frac{k_B T}{h} \frac{q_{tot,A-B}}{q_{tot,A}q_{tot,B}} e^{-\frac{E_A}{RT}}.$$

$E_A$ is the activation energy and it should be calculated taking the difference of zero of energies of transition state and reactants:

$$E_A = (\varepsilon_{0,A-B} + \varepsilon_{ZPVE,A-B}) - (\varepsilon_{0,A} + \varepsilon_{ZPVE,A} + \varepsilon_{0,B} + \varepsilon_{ZPVE,B}).$$

It should be noted that the imaginary frequency is and can not included in the calculation of the vibrational partition function and its contribution to the thermal energy is considered to be zero. On can imagine that vibrational mode corresponding to transition state has extremely small force constant, which must be neglected. In order to calculate the

\(^6\)According to [141]: For nonideal systems we may calculate $K_p$ from measured equilibrium compositions. However, then $K_p$ is not equal to $K_a$ determined from thermodynamic data.
complete partition function, one has to use the above expressions for individual partition functions and simply multiply them:

\[ q_{\text{tot}} = q_{\text{nucl}} q_{\text{elect}} q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} \]

According to Born-Oppenheimer approximation and with no excited states allowed, both \( q_{\text{nucl}} \) and \( q_{\text{elect}} \) are multiplicative constants (usually unity). Again, arranging translational partition function is such a way that it has a unit of \( 1/m^3 \), one gets appropriate unit for second order reaction rate constant.

The derivation of the whole expression can be found very detailed in chemical kinetics textbook [127], where also more complicated - but less accurate - case of kinetics in solution is treated. In rate expression for reaction in solvents, diffusion of reactants through the solvent to each other must be accounted for.

**B.4 Usage of different software packages**

General procedure for calculation of physical quantities of all molecules involved in the chosen (reaction) system comprise the following steps:

- prepare input, i.e. generate atomic coordinates;
- consider conformational analysis (using e.g. molecular mechanics) where applicable;
- preoptimise a molecule by a non-expensive (e.g. semiempirical) method;
- choose a quantum chemical method, a basis set, set charge and spin, take in account the solvation method if desired;
- start calculation to find the minimum or other desired energy structures;
- submit minimised structure to calculation of vibrational spectrum;
- extract data from output files;
- use these data as input for statistical thermodynamics analysis.

**Input file**

Specifying the atomic positions of molecules of interest can be performed either in cartesian or internal coordinates, so called Z-matrix [155]. Preparing input from “scratch” is practical only for very small molecules. Today, several graphical tools that enable the generation of atomic coordinates (e.g. Molden [327]) are available.

Most programs for quantum chemical calculation provide their own graphical user interface (e.g. Spartan GUI for Q-Chem, GaussView for Gaussian, MS Visualiser for DMol³). For the exchange of data between different programs program Babel [328] can be used. The most widely interpreted format is the “protein data base” (PDB) format.
Conformational analysis and preoptimising

Conformational analysis and the first geometry preoptimisations of given molecules can be performed by molecular mechanics (MM) methods that are based on force fields like MMFF, UFF, AMBER etc. Force field is a set of parameters in energy expression for molecular mechanics that consists of simple algebraic equations. Parameters are obtained experimentally through spectroscopic data or \textit{ab-initio} calculations. MM methods were developed for organic or biological molecules and usually cannot be applied to transition metal complexes. The application to inorganic compounds is not reasonable at all, except in cases where the parameter set was developed and trained for the particular purpose. In this case, semiempirical (SE) methods like PM3 or PM5 should be applied. Whereas MM methods do not use a wave function in energy expression, SE methods use empirical parameters and wave function. They are therefore less sensitive to the parameterisation. Semiempirical methods can be applied to inorganic systems with great inaccuracies.

The main goal of preoptimisations and further optimisations is to calculate the possibly global energy minimum on the multidimensional potential energy surface (PES) of the given molecule. This minimum corresponds to equilibrium atomic positions (geometry) according to the energy expression of the chosen method. The better the preoptimisations, the faster are the subsequent calculations in production runs [329].

B.4.1 Setting up jobs per GUI

Q-Chem (Spartan), DMol$^3$ (MS Visualizer) and Gaussian (GaussView) have - in that order - a very user friendly GUIs (graphical user interfaces) that give access to most of the features needed for engineering purposes. In contrast, Turbomole is has an interactive, command line driven GUI called “define” and requires additional software for generation of atomic coordinates. In this work, Spartan was mostly used for input preparation. The data can be exported in pdb format and read in with GaussView or MS Visualizer. GaussView exports both sybylmol2 format that can be read in Spartan and xyz format that can be imported in Turbomole. MS Visualizer also exports pdb format files.

The operations within GUIs (setting up task, computational group and model, basis set, pseudopotential, charge, spin, symmetry, etc.) are intuitively straightforward and follow the same general flow diagram for any electronic structure calculation [330]. For special features and details one has to refer to reference manuals$^7$.

Spartan and GaussView can set up jobs with coordinate driving subroutine, ideally suited for automatical producing energy profiles. These profiles, however, do not include zero point correction. In DMol$^3$ and Turbomole this feature is currently not available. The work around is the time-consuming use of many constrained optimisations.

\footnote{Caution is needed with GaussView when working with charged molecules. The GUI will automatically try to assign charge for neutral molecule and will appropriately set spin multiplicity to doublet.}
B.4.2 Locating results

Results in Spartan are accessible only through GUI (Display/Output). Several print levels are available: in the simple output, one finds $\varepsilon_0$ and corrected values for enthalpies, default temperature being 298.15 K. Calculation must be rerun with appropriate keyword for other temperatures. Zero point energy $\varepsilon_{ZPV}$ is hidden in the property achieve.

In DMol$^3$, only one output archive is produced. Final electronic energy must be searched for - the value is located after the final Ef. The properties section $\varepsilon_{ZPV}$ and contains enthalpies for temperature window from 25 K to 1000 K in 25 K steps.

Turbomole produces a file called energy in working directory after successful geometry optimisation. The first value in the last line corresponds to $\varepsilon_0$. Frequency calculation adds vibrational data to control file in addition to the calculated hessian. The output file of aoforce or NumForce subroutine contains non-scaled zero-point vibrational energy. For complete evaluation of gas phase thermodynamics, self explained routine freeh must be run. As in DMol$^3$, one can specify temperature window. Additionally, pressure window can be given.

Gaussian produces two outputs: a text and a binary. In the text section for DFT and HF calculations, the string HF must be search for. The value after last HF is the $\varepsilon_0$. For MP2 or CCSD(T) or other calculations other strings (MP, CC) must be found. Complete thermochemistry is listed for 298.15 K and 1 bar by default after each frequency calculation. For other temperatures, the utility freqchk must be used. This program requires binary checkpoint file. When calculations are run on different platforms, the interchange of data can be done be the utility formchk producing formatted (text) checkpoint file.

B.5 Input examples for Gaussian

Gaussian program is currently the most widely used program for quantum mechanics in the academical world. It has an abundance of features [331], which must often be adjusted in the scratch input file by hand. I have decided to include some typical and representative input files into this thesis. For other programs, input generation rarely requires a direct intervention in the text input file. An exception is cosmo calculation in DMol$^3$.

B.5.1 Optimisation and frequency runs

The following input file causes a geometry optimisation with subsequent analytical frequency calculation of ethene molecule with DFT functional B3LYP using LANL2DZ basis set. Checkpoint file will be saved under ethene.chk. The calculation will be performed parallelised on 4 processors with 440 megawords memory (about 4000 MB). Molecule is neutral (charge=0) and is a singlet (multiplicity=1). Z-matrix gives the position of all atoms with respect to the first C atom. Finally, connectivity data is provided. The commands gfinput and geom are dispensable: gfinput improves the print level on basis sets of individual atoms and geom specifies explicit atom bonding.
B. ADDITIONAL INFORMATION ON MOLECULAR MODELLING

%chk=ethene.chk
%mem=440MW
%nproc=4
# opt freq b3lyp/LANL2DZ ginput geom=connectivity

ethene
0 1
C
H 1 1.07000000
H 1 1.07000000 2 120.00000000
C 1 1.35520000 3 120.00000000 2 180.00000000
H 4 1.07000000 1 120.00000000 3 0.00000000
H 4 1.07000000 1 120.00000000 3 -180.00000000

1 2 1.0 3 1.0 4 2.0
2
3
4 5 1.0 6 1.0
5
6

When restarting optimisation, one has to change opt to opt=restart and geom to geom=(allcheck,connectivity). allcheck will force the optimisation to take the geometry specification from the (binary) checkpoint file, where the last steps are saved. Analytical frequency calculation is not restartable. This is important for time limited calculations of large molecules, where it is difficult to estimate the duration of calculation. If numerical frequency calculation is desired, freq=numer must be given instead of freq. Restarting numerical frequency calculation requires freq=(restart,numer).

B.5.2 Transition state runs

The only really working solution for the transition state search is to provide structures of reactant, product and transition state. The following input file will start the search for the transition state on MP2 level with Gaussian 6-311G(d,p) basis set for the decomposition reaction of PCl$_5$ to PCl$_3$ and Cl$_2$. An important prerequisite is appropriate allocation of atoms between the three structures (matching atoms) - this can be achieved by usage of coordinate monitor within GaussView GUI. An option calcall will compute force constants at every point during optimisation (eigenvector following). Furthermore, Hessian is computed at the end automatically, and vibrational spectrum in the output will hopefully show the desired one imaginary frequency.

%chk=transitionstate.chk
%mem=440MW
%nproc=4
# opt=(calcall,qst3) mp2/6-311g(d,p)

reactant
B.5. INPUT EXAMPLES FOR GAUSSIAN

0 1
Cl
P 1 2.15589100
Cl 2 2.03856600 1 90.00000000
Cl 2 2.15589100 3 90.00000000 1 180.00000000
Cl 2 2.03856605 3 119.99999920 1 90.00000000
Cl 2 2.03856605 3 119.99999920 1 -90.00000000

product
0 1
Cl
P 1 2.06950055
Cl 2 5.02000000 1 101.73554533
Cl 2 6.19329047 1 118.77572173 3 -1.02184373
Cl 2 2.06745554 1 100.37856365 3 -105.95257007
Cl 2 2.06656743 1 99.10132376 4 152.85635231

initial guess for transition state
0 1
Cl
P 1 1.98329272
Cl 2 1.91394122 1 112.79773037
Cl 2 4.06345789 1 152.24665506 3 -2.87807908
Cl 2 1.95580418 1 107.41431965 3 -119.90653204
Cl 2 1.98276701 3 112.77259109 4 60.30246985

B.5.3 Specification of basis sets and ECPs

Input for transition metals requires specification of particularly desired basis sets and where applicable the corresponding effective core potentials. The trick to produce runnable inputs is to take care of appropriate spacing between sections.

The following input calculates a single point energy for tetraselenorhenate anion interacting with ethylene on Hartree-Fock level. Hydrogen and carbon are treated with 6-311+g(d,p) basis set (gen keyword), valence electrons of rhenium and selene are described under the first four asterisks. The corresponding Hay-Wadt LANL2DZ ECP basis set is read through pseudo=read keyword. Alternatively, pseudo=LANL2DZ can be used, but may not work for other ECPs. Here, atom positions are specified in terms of Cartesian coordinates. Please, note the spacing between lines, since the input might not be read in properly.

%chk=ReSe4Ethene.chk
%mem=220MW
%nproc=2
# hf/gen pseudo=read
interaction of ReSe4- with ethylene

-1 1
Se 1.34027753 1.67447577 -0.13365198
Re -0.38572247 -0.02152423 -0.12365198
Se 1.17127753 -1.54052423 0.93434802
Se -2.17472247 0.53747577 1.28034802
Se -0.96272247 -0.70552423 -2.28765198
C 3.07627753 0.86247577 0.70834802
C 2.97527753 -0.52852423 1.25534802
H 3.07627753 -0.56052423 2.34534802
H C 0
6-311+g(d,p)
****
RE 0
S 3 1.00
2.18500000 -1.62237300
1.45100000 1.99386470
0.458500000 0.453116600
S 4 1.00
2.18500000 1.54597520
1.45100000 -2.07589270
0.458500000 -1.19223960
0.231400000 1.22728640
S 1 1.00
0.566000000E-01 1.00000000
P 3 1.00
3.35800000 -0.23186670
1.27100000 0.745868300
0.464400000 0.463268600
P 2 1.00
0.496000000 -0.131137000
0.890000000E-01 1.05036710
P 1 1.00
0.280000000E-01 1.00000000
D 2 1.00
1.11600000 0.468988800
0.426700000 0.620959100
D 1 1.00
0.137800000 1.00000000
****
SE 0
S 2 1.00
1.03300000 -3.32240950
B.5. INPUT EXAMPLES FOR GAUSSIAN

0.652100000 3.60034620
S 1 1.00
0.166000000 1.00000000
P 2 1.00
2.366000000 -0.118552200
0.383300000 1.04143200
P 1 1.00
0.118600000 1.00000000
****

RE 0
RE-ECP 4 60
g potential
6
1 1833.81438360 -0.14971040
2 414.05894560 -1669.25557810
2 59.03495400 -346.66611290
2 11.91770940 -96.66848920
2 3.65317640 -11.07385670
2 1.27641840 -0.57985520
s-g potential
7
0 247.00230850 3.14971040
1 631.71957670 45.29699690
2 249.28004410 1116.42795850
2 84.29473150 793.64190650
2 23.04079120 318.20991930
2 4.29971110 586.31050250
2 4.09743900 -475.69041640
p-g potential
5
0 193.68977260 2.14971040
1 56.93083940 64.22957360
2 18.72276020 218.85046070
2 3.73400200 344.41891680
2 3.51274830 -260.47272670
d-g potential
5
0 126.23408240 3.14971040
1 80.70908260 46.57148680
2 42.55297140 304.38345950
2 13.40749490 157.15896520
2 3.69042280 48.57012110
f-g potential
5
B. ADDITIONAL INFORMATION ON MOLECULAR MODELLING

0 112.77864590 3.95696100
1 56.78159680 52.35867810
2 28.58319660 236.03408240
2 8.57341580 116.57872660
2 2.08927210 11.10505300
SE 0
SE-ECP 3 28
f potential
5
1 433.19313360 -28.00000000
2 83.89521570 -214.38417620
2 18.58391390 -65.69187820
2 5.39552860 -24.61539320
2 1.74743260 -2.44814970
s-f potential
5
0 202.89861930 3.00000000
1 78.38204870 62.02953900
2 35.07530370 258.85559840
2 10.87695430 118.78001530
2 2.80059410 38.23552790
p-f potential
5
0 44.30118750 5.00000000
1 20.38742060 24.79734580
2 23.18899480 63.75756400
2 7.97776640 79.05128310
2 2.29881460 22.95201830
d-f potential
5
0 73.36282630 3.00000000
1 48.38356180 22.47059070
2 25.62972110 140.54928870
2 7.17058220 63.57818350
2 1.36395380 7.07536140

B.5.4 Intrinsic reaction coordinate (IRC)

After having located transition state, its geometry must be read in and the route section for the intrinsic reaction coordinate calculation can be specified in the following manner:

```
# irc=(maxpoints=40,calcfc) rb3lyp/6-31+g(d,p) geom=connectivity
```

At the beginning, command `calcfc` directs the program to compute force constants at the first point. For highly symmetrical structures with degenerated frequencies, additional keyword `nosym` should be used.
B.5.5 Using of redundant internal coordinate definitions

In order to examine potential energy surfaces, it is sometimes useful to scan the geometries that do not correspond to minima or saddle points. Both dynamic (scan) and fixed constraints can be imposed on bonds, angles and torsion angles. In the following example, distance of one hydrogen atom (atom 2) is gradually moved from its equilibrium position away from the central carbon atom (atom 1). Here, the movement is specified to be calculated in 6 steps changing the distance by 0.1 Å.

```
%chk=radical.chk
%mem=60MW
%nproc=1
# opt=modredundant hf/3-21g

methyl radical from methane
0 1
C
H 1 B1
H 1 B2 2 A1
H 1 B3 2 A2 3 D1
H 1 B4 2 A3 4 D2

B1 1.07000000
B2 1.07000000
B3 1.07000000
B4 1.07000000
A1 109.47120255
A2 109.47120255
A3 109.47123134
D1 120.00001480
D2 119.99999260
```

In contrast to the examples above, Z-matrix variables are used instead of explicitly stated bond lengths, angles and torsion angles.

**Treatment of solvation**

There are many different solvent models. In this thesis, apart from COSMO solvation model implemented in Turbomole, one of the PCM models was used in Gaussian. In this case, for example `scrf=(iefpcm,solvent=water)` must be added to the route section of the input file. Some solvents (acetonitrile, DMSO etc.) can be stated as such (solvent=string) others can be specified by real number representing permittivity constant.
C Syntheses

C.1 Preparation of CoSalen

For the preparation of CoSalen (Bis(N,N'-disalicylalethylendiamine)-µ-aquocobalt) 0.15 mol (40.5 g) of commercially available salen (bis-(N,N'-disalicylalethylendiamin)) is finely grinded. The powder is dissolved in 600 mL of distilled water in an 2 L beaker. In order to prevent evaporation of water, the beaker should be covered with watch-glass. To the suspension 11.94 g of NaOH in form of granules are added. The mixture is brought to boiling point, whereas the complete dissolving process requires about 2 h. To the homogeneous solution 0.15 mol (37.2 g) of cobalt(II)acetate tetrahydrate in 75 mL of hot water are added accompanied by continuous stirring. Brown-red paste of high viscosity is build, which is the product. If the product shows a different colour (black or dark brown), the whole procedure must be repeated, because an inactive product has been build. In order to exclude oxygen at that stage, the pase is covered with water (ca. 60-120 mL) at room temperature. In order to allow the reaction to complete the suspension is left without stirring for 1 h. The suspension is then filtered (G3 pore size). The precipitate is washed 6 times with approx. 45 ml of water at 50°C. The solid product is again suspended in 240 ml of water and filtered. The filtrate will never be colourless. The yield is 80-90%, depending of washing. Finally, the product is dried under vacuum of 5 mbar at 110°C. The product is recommended to be stored in an oxygen free (evacuated) exsiccator. For further information original reference should be consulted [332].

C.2 Palladium Cluster Precursor Synthesis

C.2.1 Preparation of bis(η^3-allyl)di-µ-chloro-dipalladium(II)

\[
2 \text{K}_2\text{PdCl}_4 + 2 \text{CH}=\text{CHCH}_2\text{Cl} + 2 \text{CO} + 2 \text{H}_2\text{O} \rightarrow (\eta^3\text{-C}_3\text{H}_5)_2\text{Pd}_2\text{Cl}_2 + 4 \text{KCl} + 2 \text{CO}_2 + 4 \text{HCl}
\]

Procedure: A 1 L two-necked, round-bottomed flask equipped with a magnetic stirring bar, a gas inlet tube and a bubbler is charged with palladium(II) chloride (24.5 g, 138 mmol) and potassium chloride (20.6 g, 276 mmol) in 300 mL of H_2O. Suspension is heated to 60 °C and stirred to yield dark red-brown solution. 300 mL of methanol and allyl chloride (28.3 g, 370 mmol) are added and the suspension is stirred for half an hour. Carbon monoxide is passed slowly (one bubble per two seconds) under stirring through the suspension for two and a half hours until the colour changes from dark red-brown to yellow-black. Methanol is evaporated at room temperature and 10⁻³ bar. The product is extracted with chloroform, washed with water and dried with sodium sulfate(VI). The
extract is filtered through the celite®. Evaporation under reduced pressure (10⁻³ bar) gives yellow crystals. Yield 20.5 g (81%).

Properties: The air-stable, yellow, crystalline compound is soluble in chloroform, benzene and tetrahydrofuran. The ¹H NMR spectrum (CDCl₃) shows signals at δ 3.06 ppm (anti CH₂, doublet, J = 12.0 Hz), 4.13 ppm (syn CH₂, doublet, J = 6.9 Hz) and 5.48 ppm (CH, complex) in a relative ratio of 2 : 2 : 1. The ¹³C NMR spectrum (CDCl₃) shows two singlets at δ 63.385 ppm (CH₂) and 111.59 ppm (CH).

C.2.2 Preparation of (η³-allyl)(η⁵-cyclopentadienyl)palladium(II)

(η³-C₃H₅)₂Pd₂Cl₂ + 2 LiC₅H₅ → 2 Pd(η³-C₃H₅)(η⁵-C₅H₅) + 2 LiCl

Procedure: Reactions and manipulations are conducted under argon atmosphere using standard Schlenk-line techniques.

A tetrahydrofuran (THF) solution of lithium cyclopentadienide (LiCp) is prepared by adding butyllithium (BuLi) (21 mL 2.5 M, 52.5 mmol) slowly to a solution of freshly distilled cyclopentadiene (Cp) (6.0 g, 91.2 mmol) in THF (120 mL). Before adding BuLi, the solution must be cooled down to -15 °C. After the reaction is completed, the pink-yellow solution is allowed to warm up to the room temperature. To prevent white solid falling out, more THF is added. Bis(η³-allyl)di-m-chloro-dipalladium(II) (9.92 g, 27.1 mmol) is placed in a 1 L Schlenk flask equipped with a three-way stopcock, a dropping funnel and a magnetic stirring bar. The flask is evacuated and filled with argon three times. THF (300mL) and benzene (100mL) are added with the syringe, to give clear yellow solution. The flask is then cooled with an ethanol-dry ice mixture to -20 °C. The THF solution of LiCp is transferred by syringe to a dropping funnel and is then added dropwise to the cooled solution with stirring at -20 °C. During the reaction the yellow solution becomes dark red. When all of the LiCp is added, the cooling bath is removed and the temperature of the reaction mixture can reach room temperature under stirring. The solvents are then removed by evaporation under reduced pressure (10⁻³ bar) and at 10 °C. The solid residue is extracted with pentane and the extract is filtered through celite® under an argon atmosphere. The red filtrate is stored under -20 °C for two days and under -78 °C for one day for recrystallization. Red long needle-like crystals are formed. Pentane is removed by decantation and evaporation. Yield 7.5 g (65 %) first fraction, 2.1 g (18 %) second fraction, all together 9.6 g (83 %).

Properties: (η³-allyl)(η⁵-cyclopentadienyl)palladium(II) forms red, needle-like crystals that are quite unstable on air and it decompose gradually at room temperature. The compound is easily sublimed and has unpleasant odour. It is recommended to store the complex below -20 °C under argon or nitrogen. The compound is soluble in pentane and THF. The ¹H NMR spectrum (CDCl₃) shows signals at δ 2.22 ppm (2H, doublet, J = 12.0 Hz), 3.59 ppm (2H, doublet, J = 6.0 Hz) and 4.88 ppm (1H, complex) for the η³-allyl protons, and 5.73 ppm (5H, singlet) for cyclopentadienyl ring protons. The ¹³C NMR spectrum (CDCl₃) shows signals at δ 44.955 ppm (CH₂), 92.971 ppm (C₅H₅) and 93.559 ppm (CH).
C.3 Preparation of Nickel Dithietete

Preparation of Nickel tetracarbonyl

In most textbooks and even in the original paper [333], the preparation of Ni(CO)$_4$ is described as unproblematic bringing together finely ground nickel and carbon monoxide at room temperature and partial pressure of 1 bar. This corresponds more or less to the so called Mond process. However, these conditions did not yield the desired product in my attempts. Therefore, in this work the synthesis was conducted in semi-continuous way at 4.5 bar and 70°C in apparatus shown in Fig. C.1a. Firstly, commercially available nickel powder was put into a pipe of 250 mm length and 8 mm inner diameter, where it was activated with hydrogen at 4.5 bar and 350°C. The temperature was then reduced to 70°C and gas feed was changed to carbon monoxide. Massive cooling at -70°C and -40°C was performed in the product vessel and the reflux cooler with both acetone/liquid nitrogen and cryostate, respectively. The crude product was evaporated and condensed again for purification. After cooling down to the storage temperature of -18°C, the product crystallised in well formed tetrahedral habitus.

![Diagram of the apparatus for the nickel tetracarbonyl synthesis](image)

Figure C.1: The scheme of apparatus for the nickel tetracarbonyl synthesis (a) and the photograph of the apparatus during the synthesis of bis-(trifluoromethyl)-1,2-dithietene

Reaction of CF$_3$-C≡C-CF$_3$ with S$_2$

The reaction of sulfur with hexafluoro-2-butyne can be conducted in two ways. In the first procedure, the sulfur can be activated under oxidation by iodine. However, after the completion of the reaction, iodine contaminations must be removed by mercury extraction. Because of the disposal problems for mercuric products, I have decided to follow the alternative procedure [334] at one atmosphere.

A 2-necked 2 liter flask containing approx. 250 g of sulfur was purged with nitrogen. The sulfur was then heated to reflux using quartz sand heater at 550°C. No reflux cooler...
was used (Fig. C.1b), since the cooling on the walls of the flask seemed to be sufficient. Nitrogen was shut off and 25 g of hexafluoro-2-butyne was slowly introduced from the bottle into one neck of the flask using autogenous pressure of the compound. Within 10 minutes the gas phase reaction at one atmosphere was completed. The heating was turned off and the content of the flask was purged with nitrogen through the second neck into the cooling trap. The cooling trap, which was detached from the flask and connected to a smaller one, contained both sulfur crystals as well as the crude product. In order to remove the product by distillation, the trap was heated to 140°C, while the liquid product could be condensed in the smaller flask. The yield was 12 g (24%).

Preparation of Nickel-dithiete

In the preparation of Nickel-dithiete the original procedure was followed [215]. The reaction was accomplished by dissolving of Ni(CO)₄ in n-pentane. This mixture was joined under cooling with the product obtained in the previous section. CO gas evolved, however, ¹³C NMR spectrum gave unambiguously no characteristic carbon peaks in the final sample. The synthesized product is probably NiS. All the organic components were removed by evacuation.

C.4 Preparation of carrier ionic liquid [BMIM]⁺[CuCl₂]⁻

The synthesis of the ionic liquid [BMIM]⁺[CuCl₂]⁻ is straightforward, although care has to taken about stoichiometry. Like tetrachloroaluminate based ionic liquids, chlorocuprate ions also tend to build associates like [Cu₂Cl₃]⁻. In this work, I have decided to synthesize the 1:1 product. Since the commercially available [BMIM]⁺Cl is highly hygroscopic and CuCl and the product are considerably oxygen/air sensitive, the Schlenk technique was used for the protection of the materials.

A glass flask with two muzzles is equipped with the magnetic rod and is located above a magnetic stirring device. One of the muzzles is connected to the nitrogen gas supply. The other muzzle is partially closed by a glass cap, which permits nitrogen to exit. Through this muzzle, firstly, the 31.92 g of [BMIM]⁺Cl are introduced into the flask against the nitrogen stream („counter-current” protective gas technique). 18.09 g of CuCl are put into the flask in the same manner. Solid mixture rapidly begins to liquify. In order to accelerate the reaction it is recommended to stir the mixture under heating (by e.g. the heating blower). After approximately 15 minutes, the heat source is removed, maintaining the stirring for approximately five hours under vacuum. The yield is quantitative (50 g of [BMIM]⁺[CuCl₂]⁻).

After a few days of storage under inert atmosphere, about 1 g of greenish precipitate is build, which however does not seem to change the properties of the bulk liquid. If the contents of the flask is open to the atmosphere, a relatively firm solid red coloured film is formed on the surface.
### Table D.1: Ideal solubility data for different gases and vapours in an ideal solvent at 25°C and 1 bar

<table>
<thead>
<tr>
<th>solvent</th>
<th>$x_{i,l}$</th>
<th>solvent</th>
<th>$x_{i,l}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0,0004</td>
<td>N₂O</td>
<td>0,0180</td>
</tr>
<tr>
<td>N₂</td>
<td>0,0010</td>
<td>C₂H₆</td>
<td>0,0250</td>
</tr>
<tr>
<td>CO</td>
<td>0,0013</td>
<td>CH₄</td>
<td>0,0350</td>
</tr>
<tr>
<td>O₂</td>
<td>0,0013</td>
<td>NH₃</td>
<td>0,1280</td>
</tr>
<tr>
<td>Ar</td>
<td>0,0016</td>
<td>SO₂</td>
<td>0,2470</td>
</tr>
<tr>
<td>NO</td>
<td>0,0020</td>
<td>C₄H₁₀</td>
<td>0,4100</td>
</tr>
<tr>
<td>CO₂</td>
<td>0,0170</td>
<td>C₂H₄</td>
<td>0,0170</td>
</tr>
</tbody>
</table>

### Table D.2: Solubility data for nitrogen, oxygen, propane and propylene in different solvents at 25°C and 1 bar ($λ_i$ in Nm³/atm; $H_i$ in bar and $x$ without unit)

<table>
<thead>
<tr>
<th>solvent</th>
<th>Nitrogen</th>
<th>Oxygen</th>
<th>Propane</th>
<th>Propylene</th>
<th>notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>0,09</td>
<td>0,168</td>
<td></td>
<td></td>
<td>$\lambda_i$</td>
</tr>
<tr>
<td>Methanol</td>
<td>4,37</td>
<td>2,43</td>
<td></td>
<td></td>
<td>$H_i$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0,279</td>
<td>0,172</td>
<td>9,7</td>
<td>15</td>
<td>$\lambda_i$</td>
</tr>
<tr>
<td>Water</td>
<td>0,0162</td>
<td>0,0313</td>
<td>0,0322</td>
<td>0,113</td>
<td>$\lambda_i$</td>
</tr>
<tr>
<td>DMSO</td>
<td>0,822</td>
<td>1,55</td>
<td>53,19</td>
<td>106,95</td>
<td>$x_i \cdot 10^4$</td>
</tr>
<tr>
<td>Benzene</td>
<td>0,123</td>
<td>0,212</td>
<td>16,2</td>
<td>21,25</td>
<td>$\lambda_i$</td>
</tr>
</tbody>
</table>
Figure D.1: Solubilities of propane and propylene in different ionic liquids: data is consistent and gives linear dependencies, i.e. Henry coefficients (here given as slopes of the lines in unit mbar m$^3$/mol) are not dependant on concentration in a given concentration range.
Nomenclature

Abbreviations

6-31+G(d) generally known form of (Gaussian) basis set
A, B, C, AB,... species in an exemplary chemical reaction (educts)
AB adduct (product)
AER all electron relativistic treatment of the atoms core electrons
ATP Adenosintriphosphate
avg average
BP, BLYP, B3LYP functionals in DFT
C\textsubscript{2}, C\textsubscript{3}, C\textsubscript{n} hydrocarbons with 2, 3, n carbon atoms
CA carrier
CAD computer aided design
CAS Chemical Abstracts Service
CF with respect to the the convective flux
corr corrected
COSMO conductor-like screening model
CPU central processor unit
CSM Carbon Molecular Sieves
CVFF consistent valence force field
CX propylene-carrier complex
DE differential equations
DEA diethanolamine
def-TZVP, SV(P) basis sets in Turbomole
DFT Density functional theory
DFT-SCP DFT optimised semicore pseudopotential treatment for core electrons
DMSO dimethylsulfoxide
DND, DNP numerical basis set functions
DOF Degrees of freedom
DSC differential scanning calorimetry
ECP effective core potentials
EDTA ethylenediaminetetraacetic acid
eff effective
ELM Emulsion Liquid Membrane
F Feed
FE, FEM finite elements method
FF force field
g, l refers to species in gas and liquid phases
GGA  general gradient approximation
GTO  Gaussian type orbitals
GUI  graphical user interface
Hartree (Ha)  atomic energy unit (1 Ha = 2625.5 kJ/mol) [a.u.]
HF  Hartree-Fock ab-initio methods
HOMO  highest occupied molecular orbital
HSAB  hard and soft acids and bases
i,j  chemical species i and j
(IEF-)PCM, CPCM  continuum solvation models (CSM) [184]
IL(s)  ionic liquid(s)
ILM  Immobilized Liquid Membrane
inert  inert component/species
L  indicates membrane interface position (permeate)
LANL2DZ  basis sets for transition metals
LC  inductance - capacity
LDA  local density approximation
LR  left-right decomposition of equation
LST, QST  linear, quadratic synchronous transit (TS search)
LUMO  lowest unoccupied molecular orbital
m, M  Membrane
MC  Membrane Contactor
MD  Molecular Dynamics
max  maximum
MEA  monoethanolamine
mix  mixture
min  minimum
MM  molecular mechanics
MPn  Møller-Plesset ab-initio methods of n-th order
MS  molecular species
MSD  mean squared displacement [m²]
n  n-th chemical species
N  with respect to the flux
NMR  nuclear magnetic resonance
NPT  constant particle/pressure/temperature ensemble
NVE  constant particles/volume/energy/ ensemble
P  Permeate
PA  propane
PBC  periodic boundary conditions
PDA  partial and algebraic equations
PDE  partial differential equations
PE  propylene
PES  potential energy surface
prod  products
PSA  Pressure Swing Absorption
PTFE  polytetrafluoroethylene
R  reactor
react  reactants
reactive  reactive component/species
RI resolution of identity option
S0, Sc pure solvent, solvent with carrier (uncharged)
S0', Sc' pure solvent, solvent with carrier (charged)
s saturation
SCF self-consistent field
SE (AM1, PM3) semiempirical methods in quantum chemistry
SLM Supported Liquid Membrane
SLRM Supported Liquid Reactive Membrane
ST storage tank
STO Slater type orbitals
SYM with respect to the symmetry
t, tot, total component/species/contributions together
tm, TM refers to transmembrane quantity
TS transition state
UFF universal force field
vdW van der Waals
VLE Vapour Liquid Equilibrium
ZPVE zero point vibrational energy

Symbols

\( a_i \) activity of component i [-]
\( A \) area \([\text{m}^2]\)
\( c \) speed of light \([\text{m/s}]\)
\( c, c_i \) liquid phase molar concentration (component i) \([\text{mol/l}], [\text{mol/m}^3]\)
\( C^* \) complex function of variables (simple model [117, 130]) [-]
\( c_p \) heat capacity at constant pressure \([\text{J/mol K}]\)
\( d \) pore diameter \([\text{m}]\)
\( D \) Diffusion coefficient \([\text{m}^2/\text{s}]\)
\( E \) energy \([\text{J}]\)
\( E_A \) activation energy \([\text{kJ/mol}]\)
\( E_{\text{int}} \) internal energy \([\text{J/mol}]\)
\( E_{\text{tot}} \) thermal correction to energy \([\text{J/mol}]\)
\( f_i \) fugacity of component i \([\text{bar}]\)
\( G \) Gibbs free energy \([\text{J/mol}]\)
\( G^* \) absolute Gibbs free energy \([\text{J}]\)
\( G_{\text{corr}} \) thermal correction to Gibbs free energy \([\text{J/mol}]\)
\( H \) absolute enthalpy \([\text{J}]\)
\( H, H_i \) Henry coefficient \([\text{Pa}], [\text{Pa m}^3/\text{mol}]\)
\( H_{\text{corr}} \) thermal correction to enthalpy \([\text{J/mol}]\)
\( h_P \) Planck constant \([\text{Js}]\)
\( J \) diffusion flux (Fick’s 1st law) \([\text{mol/m}^2 \text{ h}]\)
\( j_{i,F/P} \) diffusive velocity (feed/permeate) \([\text{mol/m}^2 \text{ s}]\)
\( j_i \) qualitative (molar/mass/volume) membrane flux of i \([\text{mol/s}]\)
\( J_{i,\text{with/without carrier}} \) absolute molar membrane flux \([\text{mol/m}^2 \text{ s}]\)
\( J_{i,\text{with/without carrier}} \) total molar membrane flux (this work only) \([\text{mol/m}^2 \text{ s}]\)
specific volume membrane flux

reaction rate constants

Boltzmann constant

tortuosity factor

thermodynamic equilibrium constant

pressure/concentration related equilibrium constant

length of the membrane and membrane module

mass

mass flow

molecular weight

arbitrary chosen high number

molar amount, index of refraction

flux per area

(partial) pressure

permeability

vapor pressure of the pure component i

total partition function of species i

volumetric flux

atomic/molecular radius

radius (radial coordinates)

dimensionless radial coordinate

reaction rate

ideal gas constant

radii of apparatus

entropy

absolute entropy

mol fraction based selectivity (binary system)

selectivity based on flux to total flux ratio

selectivity based on ratio of individual fluxes

(absolute) temperature

length, (cartesian, axial coordinates)

time

convective velocity vector (feed/permeate)

volume

liquid molecular volume increments

velocity (of the convective flux/light)

liquid phase mol fraction of components i, j

mol fractions in permeate/feed of reactive/inert species

difference of two energy levels

change of free Gibbs reaction energy

activation enthalpy in TS

change of reaction enthalpy

change of reaction entropy

activation entropy in TS

transmembrane chemical potential difference of i
### Special characters

- **d**: derivative
- **∂**: partial differential operator
- **Δ**: symbol for finite difference
- **∇**: Nabla operator
- **f**: function
- **f**: denotes formation
- **0**: indicates membrane interface position (feed)
- **0**: indicates reference state at finite temperature
- **θ**: reference state or initial input variable
- **θ**: binary diffusivity at infinite dilution
- **∑**: summation of atomic diffusion volumes [cm³/mol]
- **∞**: infinity

### Greek Characters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>ratio of diffusion coefficients (in simple model)</td>
<td>[-]</td>
</tr>
<tr>
<td>γᵢ</td>
<td>activity coefficient of component i</td>
<td>[-]</td>
</tr>
<tr>
<td>δ</td>
<td>support thickness</td>
<td>[m]</td>
</tr>
<tr>
<td>ε</td>
<td>porosity</td>
<td>[-]</td>
</tr>
<tr>
<td>ε₀</td>
<td>absolute permittivity of vacuum</td>
<td>[-]</td>
</tr>
<tr>
<td>εᵣ</td>
<td>relative permittivity</td>
<td>[-]</td>
</tr>
<tr>
<td>ε₀</td>
<td>molecular electronic energy</td>
<td>[J/mol]</td>
</tr>
<tr>
<td>εₚ₀</td>
<td>zero point vibrational energy</td>
<td>[J/mol]</td>
</tr>
<tr>
<td>η</td>
<td>dynamic (or absolute) viscosity</td>
<td>[m²/s]</td>
</tr>
<tr>
<td>θ</td>
<td>wetting angle</td>
<td>[-]</td>
</tr>
<tr>
<td>κ</td>
<td>ratio of inner and outer annulus radii</td>
<td>[-]</td>
</tr>
<tr>
<td>μ</td>
<td>electrochemical potential</td>
<td>[J/mol]</td>
</tr>
<tr>
<td>μ₀</td>
<td>absolute permeability of vacuum</td>
<td>[-]</td>
</tr>
<tr>
<td>μᵣ</td>
<td>magnetic permeability</td>
<td>[-]</td>
</tr>
<tr>
<td>ν</td>
<td>kinematic viscosity</td>
<td>[mPa s]</td>
</tr>
<tr>
<td>ν</td>
<td>stoichiometric coefficient</td>
<td>[-]</td>
</tr>
<tr>
<td>ξ</td>
<td>extent or conversion value of reaction</td>
<td>[-]</td>
</tr>
<tr>
<td>ρ</td>
<td>density</td>
<td>[kg/m³]</td>
</tr>
<tr>
<td>σ</td>
<td>surface tension</td>
<td>[mN/m]</td>
</tr>
<tr>
<td>φ</td>
<td>association factor</td>
<td>[-]</td>
</tr>
<tr>
<td>φ</td>
<td>facilitation factor</td>
<td>[-]</td>
</tr>
<tr>
<td>φᵢ</td>
<td>fugacity coefficient at given vapour pressure</td>
<td>[-]</td>
</tr>
<tr>
<td>ϕ</td>
<td>scaling factor</td>
<td>[-]</td>
</tr>
<tr>
<td>χ</td>
<td>enhancement factor</td>
<td>[-]</td>
</tr>
<tr>
<td>Ψ</td>
<td>wavefunction</td>
<td>[-]</td>
</tr>
<tr>
<td>ωᵢ</td>
<td>vibrational mode, frequency</td>
<td>[cm⁻¹]</td>
</tr>
<tr>
<td>Ψ</td>
<td>adjustment factor for solubility</td>
<td>[-]</td>
</tr>
</tbody>
</table>
Bibliography


[238] L. Wei, T.R. Halbert, H.H. Murray, E.I. Stiefel. Induced internal electron transfer reactivity of tetrathioperrhenate(VII): Synthesis of the interconvertible dimers re₂(µ-S)₂(S₂CNR₂)₄ and [re₂(µ-SS₂CNR₂)₂(S₂CNR₂)₃] [O₃SCF₃]. *Journal of the American Chemical Society*, 112(17):6431–6433, 1900.


About the author

Mitja Medved was born on August 3 1972 in Maribor, Slovenia, where he completed comprehensive secondary education in 1991. Thereafter, he studied industrial chemistry at Graz University of Technology (TU Graz, Erzherzog-Jochann-University), Austria, specialising in biotechnology, biochemistry and food chemistry. He wrote his diploma thesis in the field of chemical engineering at Bayer AG, Leverkusen, Germany in 1998. He graduated from TU Graz later in 1998. He joined the membrane technology research group of Prof. Thomas Melin at the Institut für Verfahrenstechnik of Aachen University of Technology, RWTH Aachen in 1999. In 2005 Mr. Medved decided to continue his research work at Friedrich-Alexander University in Erlangen, Germany, joining the chemical reaction engineering group of Prof. Peter Wasserscheid at the Lehrstuhl für Chemische Reaktionstechnik.