



Intra- and inter-molecular interactions in choline-based ionic liquids studied by 1D and 2D NMR

Emmanouil Veroutis^{a,c,*}, Steffen Merz^a, Rüdiger A. Eichel^{a,b}, Josef Granwehr^{a,c}

^a Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research - Fundamental Electrochemistry (IEK-9), 52428 Jülich, Germany

^b RWTH Aachen University, Institute of Physical Chemistry, 52062 Aachen, Germany

^c RWTH Aachen University, Institute of Technical and Macromolecular Chemistry, 52062 Aachen, Germany

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ABSTRACT

Choline acetate $[\text{Ch}]^+[\text{OAc}]^-$ and choline trifluoroacetate $[\text{Ch}]^+[\text{TFA}]^-$ mixed with 30 wt% H_2O have been characterized by variable temperature 1D and 2D $^1\text{H}/^{19}\text{F}$ NMR. It was found that the cation, anion and water molecules participate in a strong local H-bond network, but there was no evidence for the formation of large clusters of ions. Weaker association effects were observed for the trifluoroacetate than for the acetate, originating from the higher anion acidity of TFA. Rotational correlation times, which were extracted by temperature dependent spin-lattice relaxation measurements, indicated that cations, anions and H_2O exhibit collective reorientation even at room temperature. At the same time, no significant long-range correlations in the translational motion of the ions could be observed from PFG diffusion measurements. Moreover, 1D and 2D NOE experiments showed that both ions share close proximity to water molecules for a period on the order of 0.2 s at room temperature. It is deduced that the ions exist in a solvent-shared ion pair (SIP) configuration, with strongly correlated short-range dynamics between the choline cation and the H_2O molecules, indicating a similar behavior of these ILs to a deep eutectic solvent with water as Lewis acid. A reason for this observation, which is supported by a high entropy term in the activation process particularly at low temperatures, could be a fairly static configuration with water near the $-\text{N}(\text{CH}_3)_3$ center of the choline, and relaxation caused by pseudorotation due to reordering of the H-bond network.

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1. Introduction

In recent years, ionic liquids (ILs) have been of increased interest due to their unique physicochemical characteristics, such as thermal/chemical stability, low melting point, high ionic conductivity, or low volatility [1–3]. Another intriguing feature of ILs is that they offer high tunability in the sense that different combinations of ionic species can be used to meet specific requirements, hence the name “task specific ionic liquids” (TSILs) has been introduced by some authors [4–7]. Generally, ILs are described as salts with melting points below 100 °C, while the term “room temperature ionic liquids” (RTILs) is assigned to ILs with melting points below 25 °C. In this manuscript the more generic term “IL” will be used. ILs have been proposed as, e.g., alternatives to volatile organic solvents for chemical reactions and catalysis [8], as industrial lubricants or sealants [9], or for electrochemical applications as alternatives to the traditional electrolytes for fuel cells [10], batteries [11] and supercapacitors [12].

Traditional ionic liquids tend to incorporate cations such as imidazolium or pyridinium that suffer from high toxicity, poor biodegradability and high cost [13]. Choline, which is part of vitamin B₄ and is present at high abundance in many plants and animal organs as a constituent of lecithin, has been proposed as a more environmentally friendly and low cost alternative [14–16]. Cholines are a class of water soluble quaternary ammonium salts containing a *N,N,N*-trimethylethanolammonium (2-Hydroxy-*N,N,N*-trimethylethan-1-aminium) cation and an anion that can be adapted to produce a variety of ILs [4]. The most prominent example is choline chloride $[\text{Ch}]^+[\text{Cl}]^-$. Mixed with either a metal chloride or with a hydrogen bond donor such as an amine or a carboxylic acid, it forms a so-called “deep eutectic solvent” (DES) [17,18].

It has been found that mixtures of an IL or a salt with a suitable solvent can optimize the properties required for electrochemical applications [19–21]. In those cases, besides the solvent type, the IL/solvent molar fractions also need to be considered in order to achieve desired properties such as high ionic conductivity, low viscosity and a wide electrochemical window [22–24]. For example, Liu *et al.* examined the electrodeposition of zinc films from mixtures of 1-butyl-1-methylpyrrolidinium and 1-ethyl-3-methylimidazolium with water [25]. It was found that water fraction and temperature have a significant effect on the morphology of the Zn deposits and the electrochemical

* Corresponding author at: Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research - Fundamental Electrochemistry (IEK-9), 52428 Jülich, Germany.
E-mail address: e.veroutis@fz-juelich.de (E. Veroutis).

windows of the ILs, which was explained as originating from cation–anion and cation/anion–water interactions. They further observed that above 40 wt% water the solution changed from ionic liquid-like to aqueous-like and the electrochemical windows started to decrease.

In systems such as ILs and IL/solvent mixtures, intra- and inter-molecular interactions are important for understanding the physico-chemical characteristics [26,27]. Several studies of ionic solutions have found that not only Coulombic interactions, but also intra- and inter-molecular hydrogen bonds play an important role [28–30]. It was suggested that the good dissolution capabilities of some ILs are caused by the formation of strong hydrogen bonding networks or by a correlation between surface tension and hydrogen bonding [21,31]. Therefore, it is crucial to understand the origin of these interactions and their influence on the physicochemical properties of ILs.

Most studies on hydrogen bonding and molecular dynamics in choline-based IL/solvent mixtures are based on *ab initio* or molecular dynamics (MD) simulations [18,32,33]. Willcox *et al.* showed via MD that in choline acetate the hydroxyl group exhibited significant hydrogen bonding with the oxygen atoms of acetate. Even at 600 K about 67% of cholines still participated in H-bonding, although in their simulations they did not include solvent effects [34]. Nockemann *et al.* investigated the structure of choline saccharinate ($[\text{Ch}]^+[\text{Sac}]^-$) and acesulfamate ($[\text{Ch}]^+[\text{Ace}]^-$). They found that even though the two anions share similar characteristics, their H-bonding behavior was different. $[\text{Ch}]^+[\text{Ace}]^-$ showed H-bonding only between the hydroxy group of choline and the nitrogen of acesulfamate whereas $[\text{Ch}]^+[\text{Sac}]^-$ exhibited H-bonding with both nitrogen and carbonyl oxygen of saccharinate [14].

Nuclear magnetic resonance (NMR) is a technique that has been used extensively in the field of ionic liquids, not only for structure elucidation but also as a method for characterizing dynamics. It has become a standard practice to use pulsed field gradient (PFG) NMR in order to separately obtain the translational diffusion coefficients of the cation, anion and solvent molecules [35]. In particular, diffusion in conjunction with conductivity measurements has been used to determine the “degree of ion pairing” or “ionicity” [23,36–40].

Moreover, NMR relaxation techniques have been frequently used in ILs to investigate not only internal molecular motions but also collective rotations, which were found to play an important role e.g. for interacting IL–solvent molecules [19,20,26,41–45]. Furthermore, particularly in IL/solvent mixtures, intermolecular H-bonding or ionic pairing is expected to add contributions to the relaxation rates [46]. Techniques that utilize the Nuclear Overhauser Effect (NOE), which provides information about through-space proximity for intra- as well as inter-molecular functional groups [47–49], have often proven to be useful in the study of ILs, especially for characterizing inter-molecular cation, anion and solvent proximities [50–56].

Studies addressing choline-based ILs with NMR are not as widespread as for imidazolium or pyridinium ILs [57–59]. Gacira-Suárez *et al.* addressed the chemical stability of choline-based ILs loaded in carbon supports using NMR and x-ray photoelectron spectroscopy (XPS). They found that with choline methylsulfonate and 2-methylbutyrate the stability was higher than with the proline, alanine and serine anions due to stronger ionic interactions [60]. Harmon *et al.* have investigated choline halides and derivatives thereof for different amounts of H₂O [61–63]. They found a pronounced dependence of the chemical shift to the ionic strength. Furthermore, it was demonstrated that water associates in a

specific manner up to about ten H₂O molecules per choline, before the system starts to act as expected for a dilute solution.

Using DFT simulations, this was later proposed to be originating from a specific configuration that the water molecules attain, with one water molecule preferably located at the triangular face formed by the *N*-methyl groups, and nine H₂O molecules in a ring-like structure surrounding the choline around the $-\text{N}(\text{CH}_3)_3$ [64]. Furthermore, NMR has been used by D'Agostino *et al.* to characterize molecular motions in choline-based DES and found that for ethaline, glycine and reline the measurements correlated with the molecular weights and the extent of H-bonding, whereas for maline the opposite was observed due to formation of malonic acid dimers [65].

In this study, NMR is used to investigate mixtures of choline acetate ($[\text{Ch}]^+[\text{OAc}]^-$) with 30 wt% water and of choline trifluoroacetate ($[\text{Ch}]^+[\text{TFA}]^-$) with 30 wt% water in detail. Such mixtures have recently been demonstrated as electrolyte for rechargeable metal–air batteries [66–69]. Liu *et al.* found that a zinc–air battery–supercapacitor hybrid using an electrolyte of zinc acetate/choline acetate with 30 wt% water showed a long cycle life, with about 86% capacity retention after 1000 cycles [68,69]. To enable a more fundamental understanding of the underlying structural and dynamics features, in the present paper temperature dependent NMR spectra were recorded in order to assess the effects of concentration, chemical exchange and H-bonding. Furthermore, to probe the associated and non-associated dynamics of the different species in the mixture, temperature dependent spin–lattice relaxation measurements were conducted. Additionally, 1D and 2D ¹H Nuclear Overhauser Effect Spectroscopy (NOESY) and rotating frame Overhauser Effect Spectroscopy (ROESY) NMR [70,71] at various temperatures were employed to characterize intra- and inter-molecular proximities. Based on these observations a model for the ionic liquid/water mixtures is proposed.

2. Experimental details

2.1. Materials

Choline acetate ($[\text{Ch}]^+[\text{OAc}]^-$) (≥98%) and choline trifluoroacetate ($[\text{Ch}]^+[\text{TFA}]^-$) (≥97%) salts mixed with 30 wt% H₂O were obtained from IoLiTec GmbH (Heilbronn, Germany) and used without further purification. Correspondingly the number of H₂O per $[\text{Ch}]^+[\text{OAc}]^-$ and $[\text{Ch}]^+[\text{TFA}]^-$ was about 3.9 and 5.2 respectively. Further physicochemical properties of the mixtures are listed in Table 1. About 1 mM of 3-(trimethylsilyl)propionic-2,2,3,3-*d*₄ acid sodium salt (TSP-*d*₄, ≥98%, Sigma-Aldrich GmbH) was added for internal ¹H NMR chemical shift referencing and hexafluorobenzene (C₆F₆, ≥99.5%, Sigma-Aldrich GmbH) was used as an external ¹⁹F NMR chemical shift reference. Methanol-*d*₄ (MeOD, ≥99.5%, Sigma-Aldrich GmbH) was used for calibrating the temperature in the NMR experiments.

2.2. Viscosity measurements

For viscosity measurements a TA Instruments AR-G2 rheometer was used with a stainless steel cone plate spindle (Ø 60 mm, truncation 0.5°). The temperature of the sample was controlled using a Peltier plate and the sample was allowed to equilibrate for 10 min before starting the measurement. The viscosity was determined by measuring 11 points for shear rates between 100 and 1000 Hz and taking the mean. The data

Table 1

Physicochemical properties of $[\text{Ch}]^+[\text{OAc}]^-$ and $[\text{Ch}]^+[\text{TFA}]^-$ with 30 wt% H₂O mixtures, all obtained at room temperature: Density ρ (as specified by IoLiTec GmbH, Germany), η viscosity, M_w molecular weight of choline salts, χ_{salt} and $\chi_{\text{H}_2\text{O}}$ molar fractions of salt and water, cation self-diffusion coefficient D_{cation} , anion self-diffusion coefficient D_{anion} and water self-diffusion coefficient $D_{\text{H}_2\text{O}}$. Standard deviation in the viscosities was on the order of 15%. Fitting errors for the diffusion coefficients was about 0.2–0.3% and experimental uncertainty about 3%.

	ρ [g/cm ³]	η [mPa·s]	M_w [g/mol]	χ_{salt}	$\chi_{\text{H}_2\text{O}}$	D_{cation} [10 ^{−10} m ² /s]	D_{anion} [10 ^{−10} m ² /s]	$D_{\text{H}_2\text{O}}$ [10 ^{−10} m ² /s]
$[\text{Ch}]^+[\text{OAc}]^-$	1.084	30.5	163.2	0.204	0.795	0.344	0.464	1.51
$[\text{Ch}]^+[\text{TFA}]^-$	1.199	7.7	217.2	0.162	0.838	1.28	1.58	4.51

was additionally analyzed by linear regression and the viscosity (Table 1) was found to be within the error from that found by the mean.

2.3. NMR measurements

All NMR experiments were performed on a Bruker AvanceIII-HD spectrometer operating at 600 MHz ^1H frequency, equipped with a 5 mm BBO-H/F-Z Gradient diffusion probe (max. 17 T/m at 60 A). Temperatures were regulated using a variable temperature unit (VTU) by flowing dry nitrogen gas through the sample tube. For low temperature measurements a heat exchanger immersed in liquid nitrogen was used to produce cold nitrogen gas. Temperatures were held constant within ± 0.3 K and each sample was allowed to equilibrate for at least 20 min before starting the measurement.

Quantitative NMR spectra were obtained using hard 90° pulses with radio frequency (RF) field strength of $\nu_{\text{RF}} \sim 14$ kHz, a recycle delay of $\geq 5T_1$ and 8 accumulations for signal averaging. Spin-lattice relaxation times T_1 were measured using the inversion recovery method [72], with recovery delays varying linearly from 1 ms up to 20 s in 11 increments.

For the diffusion measurements a pulsed field gradient stimulated echo (PFGSTE) sequence was employed, with an additional longitudinal eddy current delay (LED) and two spoil gradients to dephase unwanted transverse magnetization during diffusion and LED periods [73]. Diffusional mixing and gradient lengths were fixed to 150 ms and 1 ms, respectively, and the gradient strength (g) was increased linearly from about 0.1 T/m up to 2 T/m in 16 increments. The data were fitted using the Stejskal-Tanner equation to obtain the self-diffusion coefficients [74]. The experimental uncertainty in the diffusion coefficients was found to be about $\pm 3\%$ by repeating the measurement 3 times (Table 1). Convection was established to have no effect on the measurements, attributed to the high viscosity of the samples and by comparing measurements using a 3 mm outer diameter NMR tube [75].

1D transient NOE experiments were conducted using a single PFG spin echo (SPFGSE-NOE) sequence [76] with an on-resonant 36–80 ms (adjusted for optimum sensitivity) Gaussian shaped 180° pulse for selective excitation and two gradients with $g = 82.5$ mT/m. Furthermore, a non-selective 180° pulse bracketed by two additional gradients with $g = 220$ mT/m was applied during the mixing period in order to remove residual transverse magnetization components.

The NOE build-up curves were acquired by varying the mixing times (τ_m) linearly from 4 ms up to 1 s. For the room temperature NOE experiments zero quantum coherences (ZQC) due to J -coupling were suppressed using a ~ 30 kHz frequency swept 20 ms adiabatic 180° CHIRP pulse and a ~ 60 mT/m gradient during the mixing time [77].

For spin-locking in ROESY experiments a CW pulse with RF field strength of about 2.2 kHz was employed. For room temperature measurements a phase alternating $(180^\circ \times 180^\circ \times \dots)_n$ spin-lock was used in order to suppress apparent TOCSY transfers [78]. All 1D NOE experiments were recorded using 16 accumulations and a recycle delay of 5 s.

The 2D NOESY and ROESY experiments utilized the standard gradient selected sequences with 8 scans per increment, a spectral width of 20 ppm in both dimensions and a recycle delay of 5 s [79,80]. To minimize spin diffusion effects in the low temperature 2D experiments, mixing times of $\tau_m \ll 0.5T_1$ were used [81]. Frequency discrimination in the indirect (F1) dimension was achieved using the STATES-TPPI method with 256 points zero filled to 4 k and in the direct (F2) dimension 2 k points zero filled to 4 k. Shifted sine-bell (SSB=2) QSINE multiplication was used for processing in both dimensions with subsequent polynomial baseline correction [82].

3. Results and discussion

3.1. Temperature dependence of $^1\text{H}/^{19}\text{F}$ chemical shift and linewidth

Fig. 1 shows the ^1H NMR spectrum of choline acetate ($[\text{Ch}]^+[\text{OAc}]^-$) mixed with 30 wt% H_2O at 297 K and 245 K. Furthermore, ^1H and ^{19}F

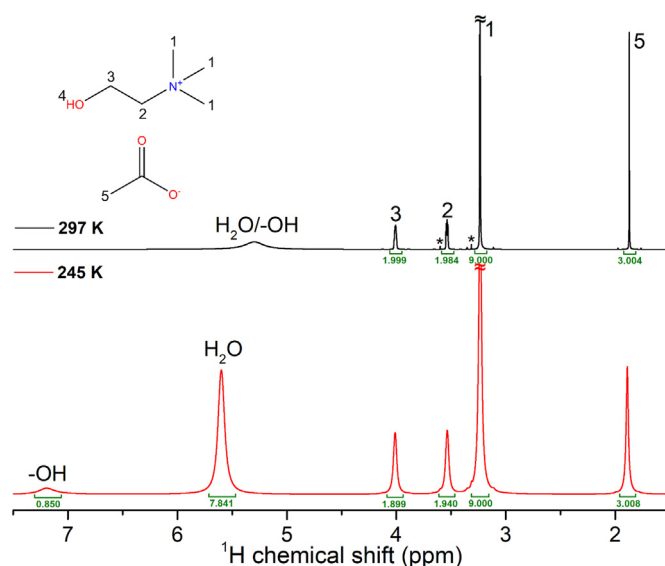


Fig. 1. ^1H NMR spectrum of $[\text{Ch}]^+[\text{OAc}]^-$ with 30 wt% H_2O at 297 K (upper, —) and at 245 K (lower, —). Normalized integrals correspond to the number of protons which are indicated by the numbers in green. Resonance assignments are indicated by the numbers, with chemical shifts reported relative to internal TSP-d4 at 0 ppm. Asterisks indicate impurities.

NMR spectra for choline trifluoroacetate ($[\text{Ch}]^+[\text{TFA}]^-$) can be found in the supporting information (Fig. S2, S3). Both the position and the width of the resonances are found to be temperature dependent. At room temperature, the ^1H resonances of $-\text{OH}$ and H_2O are not separated due to proton exchange, as discussed below.

Compared to free water with a chemical shift of $\delta = 4.8$ ppm at 297 K [83], H_2O in $[\text{Ch}]^+[\text{TFA}]^-$ shows a smaller deviation with $\delta = 4.74$ ppm than H_2O in $[\text{Ch}]^+[\text{OAc}]^-$ with $\delta = 5.3$ ppm. This is consistent with findings based on DFT calculations that stronger H-bond interactions lead to a more downfield shifted NMR resonance [84] and is correlated with differences in the acidities of the $[\text{OAc}]^-$ and $[\text{TFA}]^-$ [85]. The same trends have been reported for $[\text{Ch}]^+\text{Cl}^-$ and $[\text{Ch}]^+\text{F}^-$, with the conjugate acid of the former anion, HCl , being a strong acid and HF being a weak acid with a similar $\text{p}K_a$ as HOAc [61]. Furthermore, also the choline hydroxy resonance is shifted downfield more strongly for $[\text{Ch}]^+[\text{OAc}]^-$ than for $[\text{Ch}]^+[\text{TFA}]^-$, indicating that the $-\text{OH}$ group of $[\text{Ch}]^+$ also contributes to an H-bond network involving the IL anion and H_2O molecules.

The chemical shifts and the full width at half maximum (FWHM) linewidth for the different resonances as a function of temperature are shown in Fig. 2. For the methyl protons of acetate (labeled “5” in Fig. 1) as well as for the methyl (1) and methylene (2,3) protons of choline only a very small temperature dependence of δ is observed (Fig. 2 (a), (c)), with resonances shifting to higher chemical shift (downfield) with decreasing temperature. The change in chemical shift for those protons lies below the detection limit set by the temperature dependence of $2 \cdot 10^{-3}$ ppm/K as reported for TSP-d4 [86].

For $-\text{OH}/\text{H}_2\text{O}$ ($\delta_{-\text{OH}/\text{H}_2\text{O}}$) of both $[\text{Ch}]^+[\text{OAc}]^-$ and $[\text{Ch}]^+[\text{TFA}]^-$ a stronger temperature dependence with a downfield shift can be observed, with two different slopes above and below about 280 K (Fig. 2 (a), (c)). A comparison between H_2O and $-\text{OH}$ shifts and linewidths is shown separately in Fig. S4 in the SI. An upfield shift for hydroxyl protons with similar temperature dependent slopes have also been observed in the sterically hindered alcohol 2,2-dimethyl-3-ethyl-3-pentanol [87], which does not indicate a dominant influence of the ionic nature of the investigated samples on the chemical shift variations. Furthermore, pure water also shows a similar temperature dependence of its chemical shift [88]. Hence this shift is likely correlated with a strengthening of H-bonds with decreasing temperature.

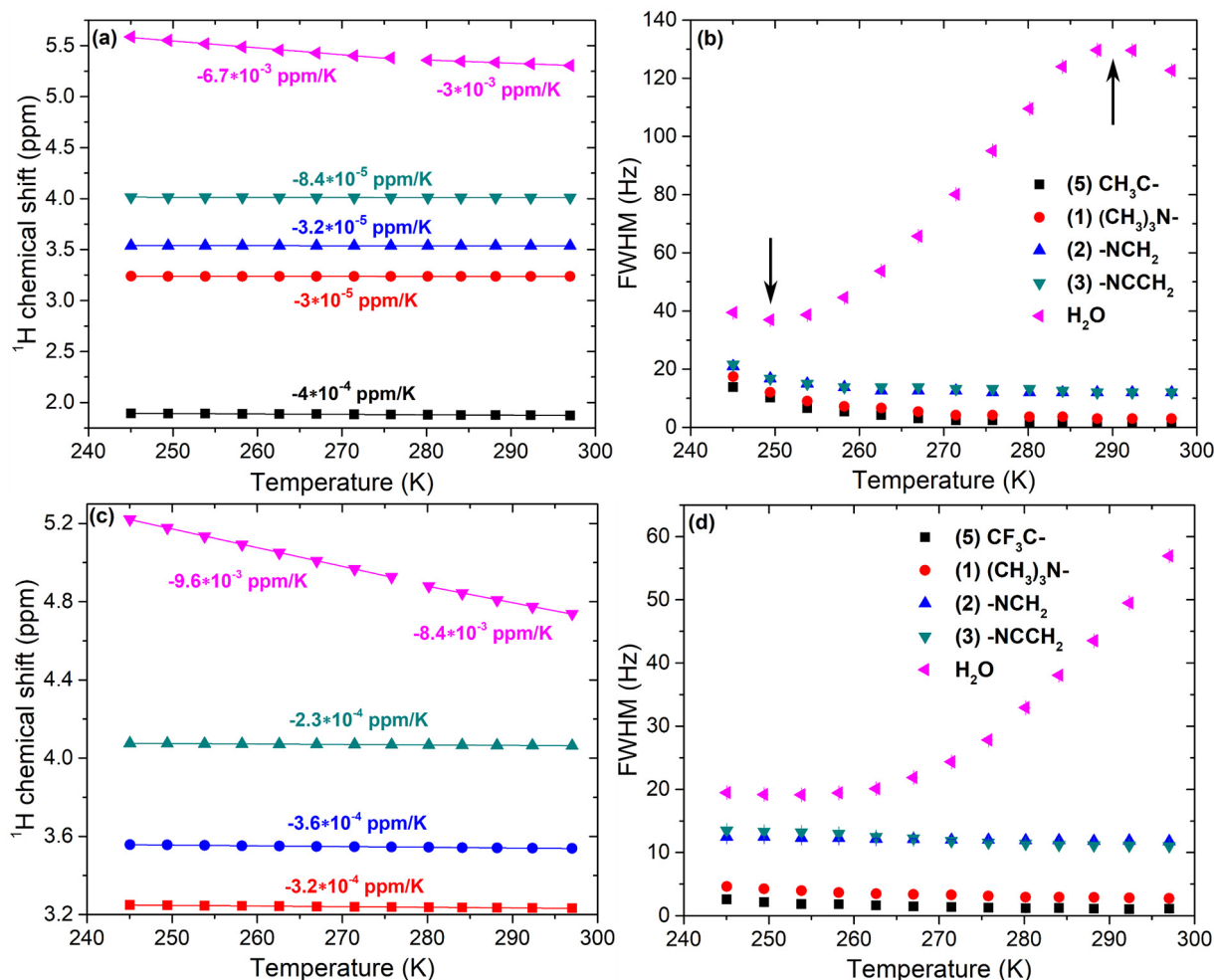


Fig. 2. ^1H chemical shift (a) and linewidth (b) as a function of temperature for $[\text{Ch}]^+[\text{OAc}]^- + 30 \text{ wt}\% \text{H}_2\text{O}$. ^1H chemical shift (c) and linewidth (d) as a function of temperature for $[\text{Ch}]^+[\text{TFA}]^- + 30 \text{ wt}\% \text{H}_2\text{O}$. Each functional group is designated by numbers in the legend corresponding to the proton assignment in Figs. 1 and S2. Colors of solid symbols correspond to each functional group and match both the chemical shift and the linewidth. Solid lines represent linear fits to the chemical shift data with their respective slopes indicated. Arrows point to the position of highest and lowest linewidth attained for H_2O . Chemical shifts are referenced relative to TSP- d_4 at each temperature.

The FWHM of $[\text{Ch}]^+[\text{OAc}]^-$ (Fig. 2 (b)) proceeds similar as a function of temperature for all cation and anion protons of the IL as well as, at low temperatures, for H_2O , which can be explained by the formation of aggregates or clusters involving all the species [89]. For $[\text{Ch}]^+[\text{TFA}]^-$ (Fig. 2 (d)) the change of FWHM for H_2O is subtle in the low temperature range, which is presumably attributed to overall weaker interactions as well as the lower viscosity. Below 250 K the linewidths of $[\text{Ch}]^+[\text{OAc}]^-$ show a concerted increase, yet the sample remains liquid. This suggests a high solvation energy for the mixture, consistent with the formation of a strong H-bond network. Such H-bond networks are well known for ILs and DES [32,90]. They can be characterized, for example, by estimating the energetics of the proton exchange processes [91]. For this purpose, the substantial temperature dependence of the proton exchange between H_2O and the $-\text{OH}$ of $[\text{Ch}]^+$ can be employed, which is apparent from the FWHM of the H_2O resonances in Fig. 2 (c), (d). The temperature range between the two arrows represents the exchange broadening region, where proton exchange leads to an increase of the FWHM, yet the resonances of the exchanging protons are still separated. Using the temperature dependence of the exchange rates the Gibbs energy $\Delta G^\ddagger$, enthalpy $\Delta H^\ddagger$ and entropy $\Delta S^\ddagger$ of activation for the proton exchange kinetics are obtained by the Eyring equation [92]. The details of the analysis are discussed in section 2.3 in the SI.

For $[\text{Ch}]^+[\text{OAc}]^-$, $\Delta H^\ddagger_{\text{H}_2\text{O}} = (26.9 \pm 0.6) \text{ kJ/mol}$ and for $[\text{Ch}]^+[\text{TFA}]^-$, $\Delta H^\ddagger_{\text{H}_2\text{O}} = (21.8 \pm 0.5) \text{ kJ/mol}$ was obtained. The value for $[\text{Ch}]^+[\text{OAc}]^-$ is

larger than for $[\text{Ch}]^+[\text{TFA}]^-$, consistent with the formation of stronger H-bonds due to reduced charge delocalization for the methyl group as compared to the trifluoromethyl group. An additional effect of the differences in the H-bond network is the viscosity variation between the two samples (Table 1). While for both samples the viscosity is

Table 2

Summary of parameters for proton exchange kinetics for $\text{H}_2\text{O}/-\text{OH}$ in $[\text{Ch}]^+[\text{OAc}]^-$ and $[\text{Ch}]^+[\text{TFA}]^-$ obtained via lineshape analysis. Exchange rate k_{ex} and Gibbs free energy $\Delta G^\ddagger$ obtained at 249.4 K, enthalpy $\Delta H^\ddagger$ and entropy $\Delta S^\ddagger$ obtained from the slope and intercept shown in Fig. S5 in the SI. For the thermodynamic parameters a transmission coefficient $\kappa=1$ was used. Errors are standard deviations from the fit and do not include systematic contributions.

	Lineshape analysis			
	Ch.OAc		Ch.TFA	
	H_2O	$-\text{OH}$	H_2O	$-\text{OH}$
$k_{\text{ex}} [\text{s}^{-1}]$ @249.4 K	78.4 ± 0.1	391 ± 3	47.5 ± 0.1	110 ± 4
$\Delta G^\ddagger [\text{kJ/mol}]$ @249.4 K	51.6 ± 0.1	48.3 ± 0.1	52.7 ± 0.1	50.9 ± 0.1
$\Delta H^\ddagger [\text{kJ/mol}]$	26.9 ± 0.6	45.1 ± 1.3	21.8 ± 0.5	40.8 ± 0.6
$\Delta S^\ddagger [\text{J/mol} \cdot \text{K}]$	-99.5 ± 2.4	-13.4 ± 5.2	-128.7 ± 1.7	-40.6 ± 2.5

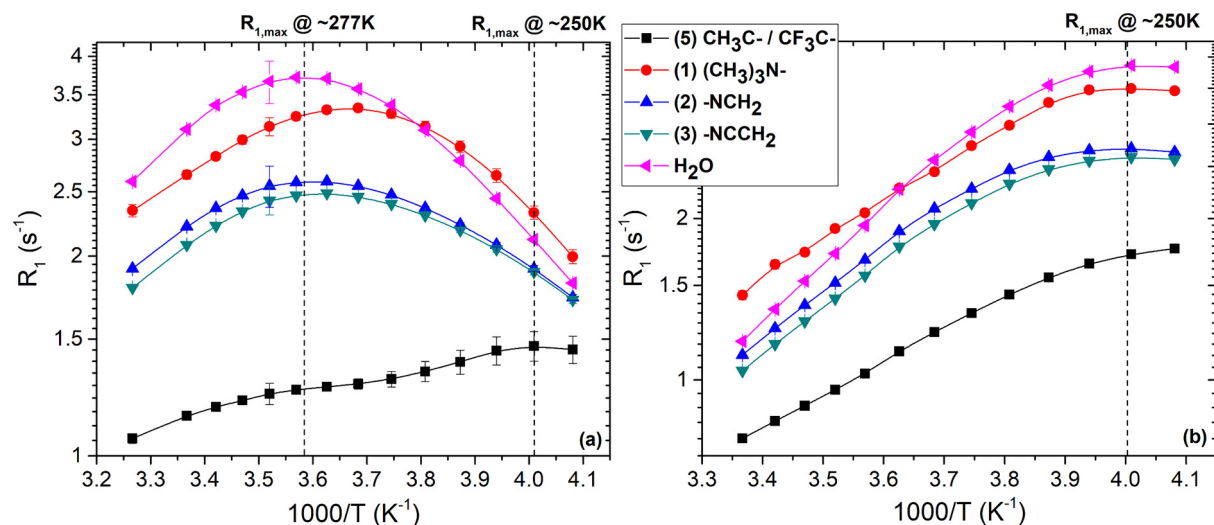


Fig. 3. Spin-lattice relaxation rates R_1 as a function of inverse temperature for [Ch]⁺[OAc]⁻ + 30 wt% H₂O (a) and [Ch]⁺[TFA]⁻ + 30 wt% H₂O (b). Dashed lines indicate the occurrence of R_1 maxima (or T_1 minima) and solid lines are guides for the eye.

considerably higher than for pure water, the viscosity of [Ch]⁺[TFA]⁻ is about a factor of four lower than the viscosity of [Ch]⁺[OAc]⁻.

Aschworth et al. classified medium strength H-bonds as those having energies between 17 and 63 kJ/mol. This is the range where most H-bonds involving ionic-neutral pairs take place, e.g. [X]⁺[Y]⁻...R, where R is the neutral molecule [18,32]. Energies above 63 kJ/mol would indicate the presence of strong ion-ion interactions, e.g. [X]⁺...[Y]⁻. Hence the obtained energies for H₂O and also -OH as discussed below, are within the range for medium strength H-bonds. Similar energies were also found by Zhang et al. using NMR, IR and DFT calculations for the interaction of [TFA]⁻...H₂O, [Bmim]⁺...H₂O and [Bmim]⁺...CH₃OH [28].

Due to the lower molar concentration of [Ch]⁺ compared to H₂O the signal of choline -OH proton is weaker and the resonance due to exchange correspondingly broader. The same procedure is followed in order to estimate the enthalpy of activation for exchange of the -OH proton. For [Ch]⁺[OAc]⁻, $\Delta H^\ddagger_{OH} = (45.1 \pm 1.3)$ kJ/mol and for [Ch]⁺[TFA]⁻, $\Delta H^\ddagger_{OH} = (40.8 \pm 0.6)$ kJ/mol was obtained. Again, the enthalpy of activation is larger for [Ch]⁺[OAc]⁻ than for [Ch]⁺[TFA]⁻. Furthermore, when comparing the difference in enthalpy of activation for the two protons $\Delta\Delta H^\ddagger = \Delta H^\ddagger_{OH} - \Delta H^\ddagger_{H_2O}$, for [Ch]⁺[OAc]⁻ a value of 18.2 kJ/mol and for [Ch]⁺[TFA]⁻ a value of 19 kJ/mol is obtained. This indicates that not only the H₂O protons, but also the choline -OH protons are stabilized by the presence of an IL anion that corresponds to a conjugate base of a weak acid, which forms a more stabilized H-bond network.

Proton exchange kinetics is either a second order process or may proceed over more complicated pathways involving intermediate states. However, from the point of view of magnetic resonance, it can be described by pseudo first order kinetics, since NMR is sensitive to the rate of proton exchange as experienced individually by each donor or acceptor [93]. Nonetheless, in case of a direct process with a single activation barrier, the activation energy is identical for donor and acceptor, no matter their ratio, since an exchange of two protons does not lead to a variation in ground state energy, and a reaction over a single barrier would require the same activation energy from either side.

The different activation enthalpies observed, indicate the presence of competing pathways or that proton exchange proceeds over multiple steps, involving activated intermediate states with a certain probability of falling back to the original state. This is consistent with the formation of a complex H-bond network that involves [Ch]⁺, [OAc]⁻ and H₂O molecules. Furthermore, the proton exchange for the -OH does not proceed in a direct step with a single activation barrier, in which case the

enthalpy of exchange should be identical to the corresponding $\Delta H^\ddagger_{H_2O}$ for each $\Delta H^\ddagger_{OH}$. Additionally, the obtained large negative entropies (Table 2) can be attributed to the increased ordering facilitated by the stabilization of the aggregate state. Such state would be stabilized by the H-bonding interactions between the individual species in the mixture.

An overview of the parameters obtained for the proton exchange kinetics of H₂O and -OH is given in Table 2. A comparison of exchange rates and Gibbs free energies between those derived from lineshape analysis and those from magnetization transfer experiments is also discussed in SI (Fig. S6 and Table S1).

3.2. Temperature dependence of ¹H/¹⁹F R_1 rates

The rotational dynamics of cation, anion and solvent molecules were probed using temperature dependent spin-lattice relaxation rates $R_1 = 1/T_1$.

In Fig. 3 (a), (b) the ¹H and, for -CF₃ of [TFA]⁻, also the ¹⁹F spin-lattice relaxation rates for each functional group of [Ch]⁺[OAc]⁻ and [Ch]⁺[TFA]⁻ are plotted as a function of inverse temperature. The similarity in the relaxation rates, both at low and at high temperature, and their dispersion behavior, with a similar maximum for all the functional groups of [Ch]⁺ as well as for the protons of H₂O, indicates that relaxation is not only induced by modulation of intramolecular dipolar interactions between nearest-neighbor protons, but that rotational motions

Table 3

Activation energies E_a for rotational motion as obtained from the linear fits in Fig. S7 for the high and low temperature regions of the relaxation rates. The low-T region for [Ch]⁺[TFA]⁻ as well as for [OAc]⁻ was not available in the recorder range.

		E_a [kJ/mol]	
		High-T	Low-T
[Ch] ⁺ [OAc] ⁻	CH ₃ C-	5.4 ± 0.4	-
	(CH ₃) ₃ N-	10 ± 0.1	15.3 ± 0.8
	-NCH ₂	10.5 ± 0.7	10.1 ± 0.5
	-NCCH ₂	10.9 ± 0.6	9.6 ± 0.5
	H ₂ O	13 ± 1	17 ± 0.2
[Ch] ⁺ [TFA] ⁻	CF ₃ C-	11.9 ± 0.1	-
	(CH ₃) ₃ N-	13.6 ± 0.4	-
	-NCH ₂	15.9 ± 0.4	-
	-NCCH ₂	16 ± 0.3	-
	H ₂ O	20 ± 0.3	-

of the species in the mixtures are correlated. The correlated dispersion of the curves is probably caused by the effects of H-bonding. The difference in the position of the maximum for the two ILs is also correlated with their difference in viscosity (see Table 1), where $[\text{Ch}]^+[\text{OAc}]^-$ tumbles more slowly than $[\text{Ch}]^+[\text{TFA}]^-$ and therefore its maximum is shifted to higher temperatures.

The temperature of the relaxation rate maxima is high for molecules of such a small molecular weight. Only the anions show a slower relaxation, yet with a maximum at a similar temperature as the cations and H_2O . According to the Bloembergen–Purcell–Pound (BPP) model [94] (Eq. (S2) in the SI), the relaxation rate maxima as shown in Fig. 3 correspond to correlation times on the order of 160–170 ps. In the temperature range covered by the experiments, these correlation times are much too large for internal group rotations. Based on Steele's inertia

model [95], Burke et al. reported correlation times for a $-\text{CF}_3$ group at room temperature on the order of 0.3 ps [96]. For a $-\text{CH}_3$ group an even shorter correlation time is expected due to its smaller mass. Therefore, internal group rotations are not the driving force for the observed phenomena. The maxima are therefore attributed to a collective reorientation of aggregates consisting of tightly associated choline and water and, to a somewhat lesser extent, also involving the anions.

The relaxation dispersion curve of the $[\text{OAc}]^-$ anion shows two different maxima, one close to the maxima of the cation functional groups and the H_2O around 277 K, and the other, more pronounced one at around 250 K. Such behavior is not visible in the case of the $[\text{TFA}]^-$ anions, where the common maximum is just within the temperature range probed. This is indicative of two different motional processes for

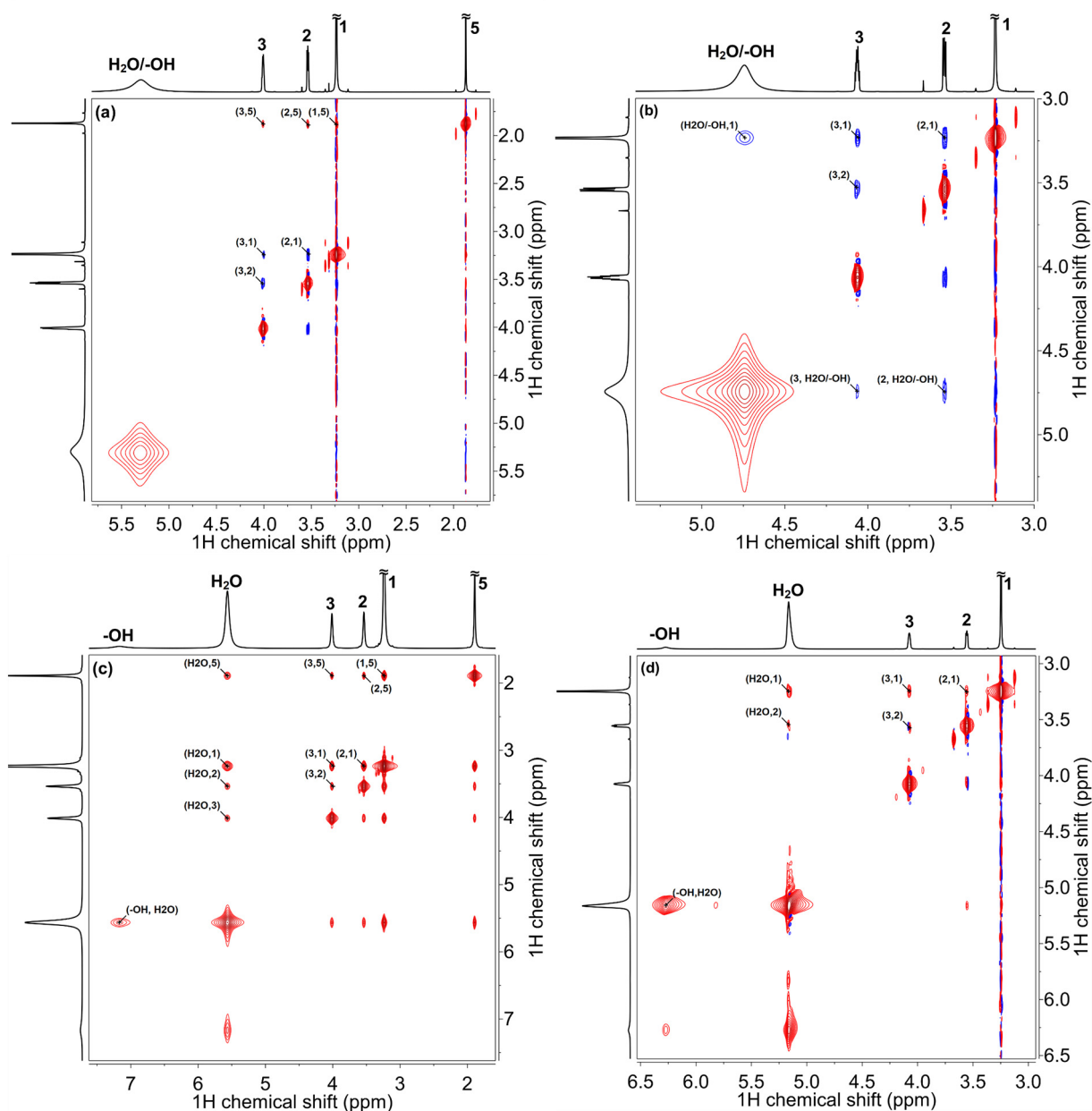


Fig. 4. 2D NOESY spectra of $[\text{Ch}]^+[\text{OAc}]^-$ (a) and $[\text{Ch}]^+[\text{TFA}]^-$ (b) at 297 K, and of $[\text{Ch}]^+[\text{OAc}]^-$ (c) and $[\text{Ch}]^+[\text{TFA}]^-$ (d) at 249.4 K. Mixing times were $\tau_m = 0.45$ s for the spectrum in (a) and 0.6 s for (b), $\tau_m = 0.05$ s for (c) and $\tau_m = 0.15$ s for (d). For the spectra at 249.4 K the mixing times were within the initial rate approximation (see chapter 1.2 in SI). Intra- and inter-molecular correlations are assigned by the numbers in parentheses corresponding to the respective protons (see Fig. 1). Cross peaks ($-\text{OH}, \text{H}_2\text{O}$) are due to chemical exchange. Spectra were scaled to maximum peak height and contours were chosen so that the weakest cross peak is visible for each panel. Diagonal peaks are phased positive (red). For the projections in the direct and indirect dimensions the 1D spectrum was used.

the $[\text{OAc}]^-$ anion, with a transition between them within the investigated temperature range.

For a more quantitative analysis, the temperature dependent R_1 data were fitted using the BPP model with a Lorentzian spectral density of the rotational motion (i.e. an exponentially decaying autocorrelation function; Eq. (S3) in the SI). It was further assumed that the correlation time τ_c can be fitted with the Arrhenius equation, Eq. (S6), (S7). If the BPP model with a Lorentzian spectral density of the rotational motion in combination with an Arrhenius model for the temperature dependence of τ_c provides a good description of the data, the R_1 curve should be symmetric with respect to the maximum. For $[\text{Ch}]^+[\text{OAc}]^-$, this kind of symmetry is not observed, with a higher activation energy in the low-temperature than in the high-temperature region, as can be seen in Table 3 below.

The difference in energy between the high and low- T regions are presumably due to strong intermolecular interactions, especially when considering the high molar concentration of H_2O present. This adds additional relaxation pathways which are not taken into account by the BPP model. $[\text{Ch}]^+[\text{TFA}]^-$ shows maxima at the lower end of the probed temperature range, hence a quantitative analysis using the symmetry with respect to the maximum cannot be conducted. Nonetheless, the similarity of the shapes for the different protons is still apparent, indicating common dynamics of the respective functional groups, yet amounting to different energies of activation at the high temperature end of the curves.

Alternatively, as detailed by Kruk et al., relaxation rates for ILs can be modeled in a similar way as for molecular liquids assuming instead a Cole–Davidson rather than a Lorentzian form [97]. This approach is based on the common observation in measurements of temperature dependent relaxation rates that the influence of magnetic interactions, commonly summarized as spin diffusion, is growing with decreasing temperature, which leads to a stretching of the relaxation rate. Such a phenomenological stretching parameter β with $0 < \beta \leq 1$, is incorporated in the Cole–Davidson spectral density.

Fitting the present R_1 data with such a model improved the residuals, yet led to $\beta > 1$, which necessarily has a different origin than spin diffusion but is in accordance with a higher E_a at lower temperature. The variation of energy within the measured temperature region suggests a transition between two different relaxation-determining motional regimes. In addition, the similarity of the data for the ^1H nuclei of the N -methyl and the water suggest concerted motions of the two. The methylene protons show similar activation energies at both high and low- T regions. Therefore, a preferred location of at least some of the H_2O molecules would be close to the N -methyl groups.

The higher activation energies at low temperature, might indicate a compensating entropy of activation for the collective reorientation process. Such entropy of activation could be caused by a pseudorotation mechanism that induces fluctuations of spin interactions by a rearrangement of the H-bond network rather than an actual physical rotation of the molecules and ions [98].

3.3. 2D NOESY spectra

NOESY experiments were conducted to probe spatial proximity ($\leq 5\text{\AA}$) over a prolonged period, on the order of 0.5 s. In addition, 2D ROESY experiments were performed (Fig. S11 in the SI) to distinguish between NOE cross peaks and exchange cross peaks, which show the same phase in the NOESY spectra if $2\pi\nu_0\tau_c > 1.12$. With ROESY, not only exchange cross peaks can be separated from NOE correlations, but false or relayed NOEs via spin diffusion can also be discriminated [80,99].

In Fig. 4 (a) and (b) the 2D NOESY spectra of $[\text{Ch}]^+[\text{OAc}]^-$ and $[\text{Ch}]^+[\text{TFA}]^-$, respectively, are compared at 297 K. Cross peaks with negative phase (blue) indicate positive proton NOE correlations (“fast tumbling” limit, see also chapter 1.2 in the SI), cross peaks with positive phase (red) indicate negative proton NOE correlations (“slow tumbling”

limit, but also chemical exchange) and mixed phase cross peaks originating from J -coupled spins [100]. Both ILs show negative phase cross peaks between the choline protons (2,1), (3,1) and (3,2), indicating positive intra-NOE correlations. In addition, weak inter-NOE cross peaks between the methyl groups of choline and $-\text{OH}/\text{H}_2\text{O}$ ($\text{H}_2\text{O}/-\text{OH}$,1) can be observed. $[\text{Ch}]^+[\text{OAc}]^-$ also experiences negative inter-NOE correlations between cation and anion (1,5), (2,5) and (3,5) at 297 K, which are also observed in the ROESY spectra (Fig. S11). These findings indicate that cation, anion and water molecules are spatially close for sufficiently long time periods that NOE correlations can evolve.

At 249.4 K (Fig. 4 (c), (d)), strong intermolecular correlations can be observed between the methyl groups of choline and the methyl of acetate (1,5) as well as between the groups of choline, acetate and the water protons (H_2O ,1–3) and (H_2O ,5). Chemical exchange between H_2O and $-\text{OH}$ is also assigned in the NOESY spectra, with cross peaks ($-\text{OH},\text{H}_2\text{O}$) for $[\text{Ch}]^+[\text{OAc}]^-$ and $[\text{Ch}]^+[\text{TFA}]^-$. All cross peaks are in phase with the diagonal peaks for both ILs, which indicates negative NOEs [47]. NOESY spectra experience a zero crossing, i.e. the absence of NOE correlations, and an accompanying change of sign at $2\pi\nu_0\tau_c \approx 1.12$. Therefore, τ_c crosses this threshold between the two temperatures presented.

3.4. 1D selective NOE

To obtain information on the NOE dynamics, 1D selective NOE experiments were recorded at different temperatures and with different mixing times. Fig. 5 shows the 1D selective NOE spectra of $[\text{Ch}]^+[\text{OAc}]^-$, with the $(\text{CH}_3)_3\text{N}-$ protons as target resonance, at different temperatures. For 306.15 K and 297 K the two methylene groups of choline ($-\text{NCH}_2$ (1,2) and $-\text{NCCH}_2$ (1,3)) as well as the $-\text{OH}/\text{H}_2\text{O}$ show positive intra- and inter-molecular NOE correlations, whereas the methyl group of acetate (1,5) shows negative intermolecular NOE correlations, as observed in the 2D NOESY and ROESY spectra. By increasing the temperature from 297 K to 306.15 K the strength of

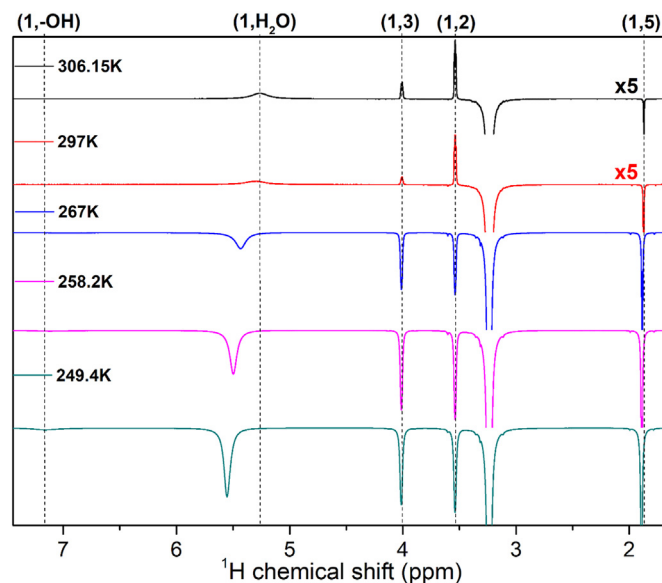


Fig. 5. 1D SPFGSE NOE spectra of $[\text{Ch}]^+[\text{OAc}]^-$ at different temperatures. Truncated signal corresponds to the selectively inverted $(\text{CH}_3)_3\text{N}-$ resonance. Dashed lines indicate NOE responses assigned as (1,5) $(\text{CH}_3)_3\text{N}- \rightarrow \text{CH}_3\text{C}-$, (1,2) $(\text{CH}_3)_3\text{N}- \rightarrow -\text{NCH}_2$, (1,3) $(\text{CH}_3)_3\text{N}- \rightarrow -\text{NCCH}_2$, (1,H₂O) $(\text{CH}_3)_3\text{N}- \rightarrow \text{H}_2\text{O}$ and (1,-OH) $(\text{CH}_3)_3\text{N}- \rightarrow -\text{OH}$. Numbers in the parenthesis correspond to the proton assignment as in Fig. 1. Mixing times were chosen so that the spectra would have approximately the highest intensity at each temperature. They were $\tau_m = 0.45$ s for 306.15 K (—) and 297 K (—), $\tau_m = 0.26$ s for 267 K (—) and $\tau_m = 0.2$ s for 258.2 K (—) and 249.4 K (—). The NOEs at 303.15 K and 296.65 K were small so the spectra were scaled by a factor of about 5 as compared to the spectra at the other temperatures.

positive NOEs increases, which is in agreement with the decrease of the rotational correlation time at higher temperatures. The negative NOE observed for $[\text{OAc}]^-$ (1,5) gets weaker as the temperature increases and almost reaches zero at 306.15 K. The fact that the choline protons and the methyl protons of acetate (1,5) change sign at a different temperature suggests that the reorientational processes responsible for the intramolecular and the intermolecular NOE correlations are similar but not identical, as also suggested by the temperature dependent relaxation rate measurements.

At 267 K, strong negative NOEs are measured for all the resonances, which is expected for $2\pi\nu_0\tau_c \gg 1$. From the relation $2\pi\nu_0\tau_c \approx 1.12$ for the zero-crossing of NOE cross-peaks, the temperature at which $\tau_c \approx 0.3$ ns can be estimated. For the intermolecular process involving NOEs between the cation methyl protons and water, (1,H₂O), this occurs below 297 K, while for the NOEs between cation methyl protons and acetate protons, (1,5), the crossover is not observed, and presumably takes place above 306.15 K. The intramolecular NOEs change their sign and evolve in amplitude approximately similar with the (1,H₂O) intermolecular NOEs over the whole temperature range probed. This is consistent with the similar reorientation dynamics for both H₂O and $[\text{Ch}]^+$ as obtained by the spin-relaxation rates. Therefore, the solvation of choline by water appears to be almost static for prolonged durations. To estimate the dynamics of these static conformations, a series of 1D SPFGSE NOE spectra have been recorded with increasing mixing time.

Fig. 6 shows the build-up curves for the intermolecular NOEs (1,5) $(\text{CH}_3)_3\text{N}^- \rightarrow \text{CH}_3\text{C}^-$ (a), (1,H₂O) $(\text{CH}_3)_3\text{N}^- \rightarrow \text{H}_2\text{O}$ (d), and for the

intramolecular NOEs (1,2) $(\text{CH}_3)_3\text{N}^- \rightarrow -\text{NCH}_2$ (b) and (1,3) $(\text{CH}_3)_3\text{N}^- \rightarrow -\text{NCCH}_2$ (c) at different temperatures. The curves show the combined effect of magnetization build-up due to cross relaxation (NOE effect) and magnetization decay due to leakage processes (external relaxation). The cross-relaxation rates obtained by fitting the data with Eq. (S9) are listed in Table 4.

For all groups the cross relaxation rates increase as temperature decreases. For intramolecular NOEs (1,2), (1,3) this reflects the increase in population probability for a particular molecular conformation. This is conceivable for $[\text{Ch}]^+$ which has a high conformational flexibility with respect to the distance between the methyl groups and the alkyl chain.

For intermolecular NOEs (1,5) and (1,H₂O) a decrease in cross relaxation rates (see also section S2.5 and Eq. (S13) in SI) is induced by the decrease in mutual self-diffusion for the interacting pairs as temperature decreases. Furthermore, the closest distance of approach between $[\text{Ch}]^+$, $[\text{OAc}]^-$ and H₂O will also decrease with temperature, because there is a higher statistical probability that the species will interact for longer periods of time and thereby inducing cross relaxation. For that matter intermolecular H-bonding will bring the species of the mixture closer and as a direct consequence the cross relaxation rate will increase [101,102].

3.5. Structural model

The presented data provide a multifaceted picture concerning the structure and dynamics of $[\text{Ch}]^+[\text{OAc}]^-$ and $[\text{Ch}]^+[\text{TFA}]^-$ / water

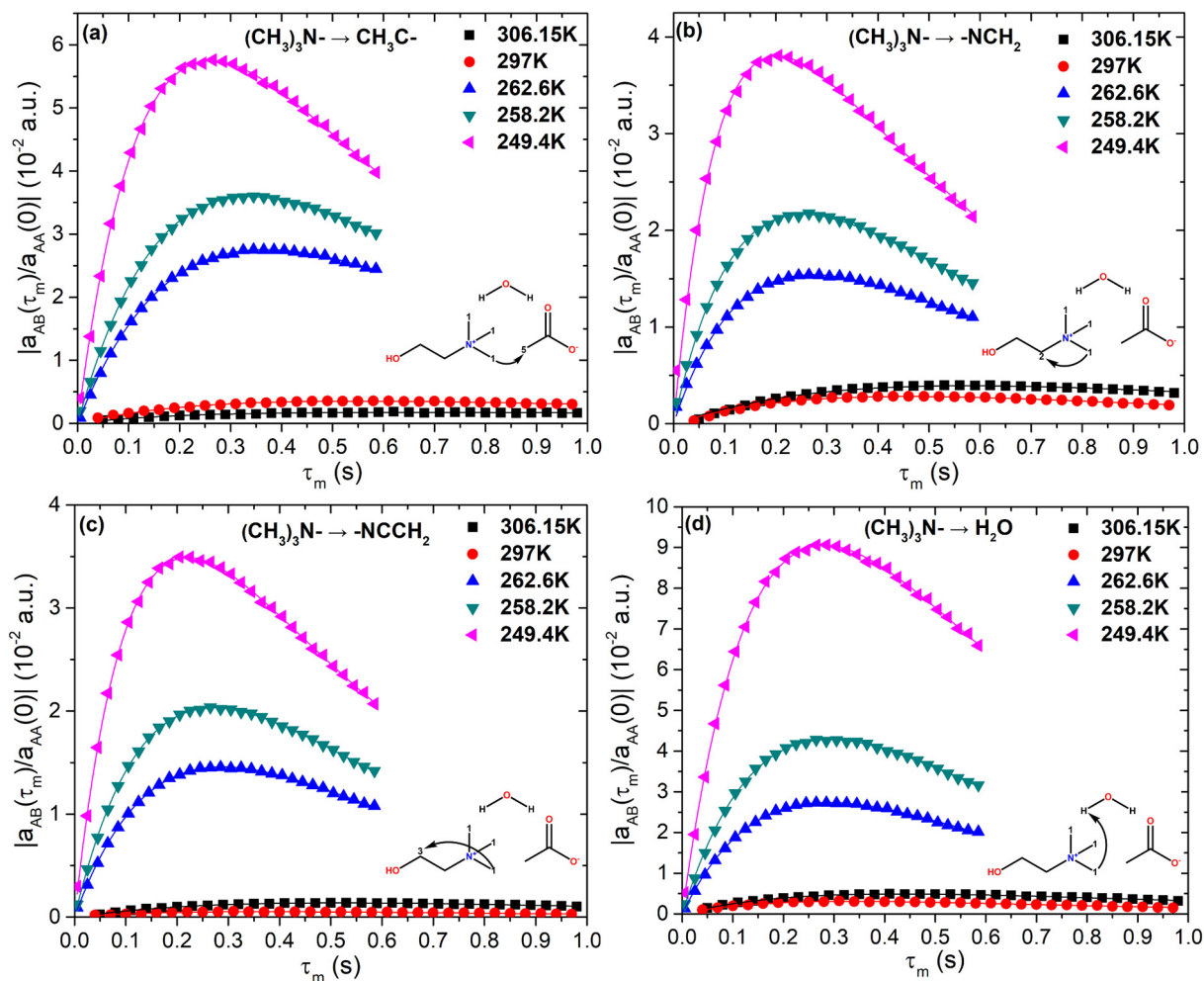


Fig. 6. Absolute value NOE build-up curves for (1,5) $(\text{CH}_3)_3\text{N}^- \rightarrow \text{CH}_3\text{C}^-$ (a), (1,2) $(\text{CH}_3)_3\text{N}^- \rightarrow -\text{NCH}_2$ (b), (1,3) $(\text{CH}_3)_3\text{N}^- \rightarrow -\text{NCCH}_2$ (c) and (1,H₂O) $(\text{CH}_3)_3\text{N}^- \rightarrow \text{H}_2\text{O}$ (d) at different temperatures. Intensities were normalized to the intensity of the $(\text{CH}_3)_3\text{N}^-$ target resonance at $\tau_m = 0$ s. Solid lines correspond to fits with Eq. (S9). NOE transfers are illustrated by the molecules in each panel.

Table 4

Cross relaxation rates σ for (1,5) $(\text{CH}_3)_3\text{N}^- \rightarrow \text{CH}_3\text{C}^-$, (1,2) $(\text{CH}_3)_3\text{N}^- \rightarrow -\text{NCH}_2$, (1,3) $\text{CH}_3^- \rightarrow -\text{NCCH}_2$ and (1,H₂O) $(\text{CH}_3)_3\text{N}^- \rightarrow \text{H}_2\text{O}$ at different temperatures, obtained by fit to the build-up curves with Eq.(S9).

T [K]	$\sigma_{\text{fit}} [10^{-3} \text{ s}^{-1}]$			
	CH_3C^-	$-\text{NCH}_2$	$-\text{NCCH}_2$	H_2O
306.15	4.4 ± 0.1	11.3 ± 0.4	4.5 ± 0.1	19.6 ± 0.3
297	8.7 ± 0.2	10.2 ± 0.3	2.5 ± 0.1	16.4 ± 0.3
262.6	90 ± 5	99 ± 2	85 ± 5	158 ± 1
258.2	130 ± 1	150 ± 2	127 ± 1	246 ± 2
249.4	280 ± 2	345 ± 6	282 ± 2	557 ± 3

mixtures which defy classification into a particular category. The primary reason is that structure and dynamics are linked, with large activation energies for rotational motions and exchange, yet sufficient flexibility to maintain considerable translational and rotational mobility even at 245 K. This leads to fairly stable structural motives, yet prevents assignment of static properties and features that would allow an exhaustive explanation of the observed data. Based on relaxation measurements, rotational correlation times and interaction strengths are very similar for cation, anions and H_2O molecules. The activation energies suggest a strong local H-bond network that involves interactions between cations– H_2O , cations–anions, and anions– H_2O , whereby the cations– H_2O interactions seem to be the most strongly correlated ones. This network leads to a stabilized local structure that is maintained over sufficiently long periods of time to enable the evolution of inter- and intra-molecular NOE correlations with similar correlation times. At the same time, long-range structural features that would be expected if large clusters would form appear to be less pronounced, suggesting an H-bond network of rather limited extent. Translational mobility is high enough for all the molecules that the formation of clusters involving multiple cations, anions or ion pairs does not appear to be particularly favorable.

The translational self-diffusion coefficients are different for cations, anions and H_2O , hence contact ion pairing (CIP) is not supported by the data (see section 2.7 in the SI) [103]. This may be caused by a sterically hindered close proximity of cation and anion, in combination with a considerable delocalization of the negative charge in the anions and a shielding of the charges by the H_2O molecules. At the same time, the evolution of NOE correlations between cation and anion protons suggest that all three components must maintain a sizable mutual contact. This indicates that anions and H_2O molecules choose selective configurations and pathways rather than unspecific solvation and motion around the cations [104]. These observations, in particular the differences in mobility between cations/water and anions would be consistent with the formation of a solvent-shared ion pair (SIP).

The formation of strong local interactions between all the components in the mixture and weaker long-range interactions prevents de-mixing and crystallization when the sample is cooled down. In the mixtures investigated here, which were selected due to their favorable performance as electrolyte for electrochemical reactions, the strong local interactions involve all the components in their stoichiometric proportions. The properties described here resemble the behavior of a eutectic mixture, which suggests the formation of a deep eutectic solvent (DES), with H_2O as Lewis acid.

The activation energies for rotation as well as for diffusion at low temperatures are high, considering the observed sizable low-temperature mobility. Such high activation energy needs to be compensated by a high entropy contribution. One possible explanation could be the formation of a long-term stable molecular arrangement of water associated with choline, where relaxation is induced by pseudorotation rather than molecular rotation.

In Fig. 7 a possible molecular arrangement is presented that depicts the main inter- and intra-NOE pathways and suggests possible H-bonds

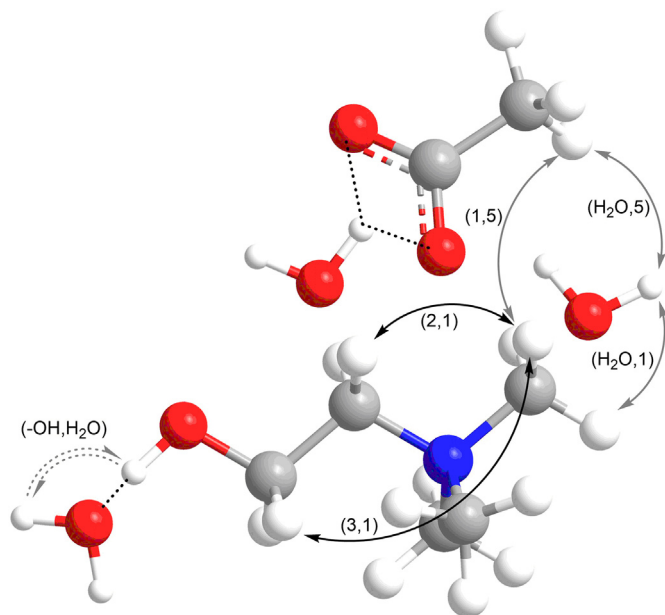


Fig. 7. Qualitative depiction of intermolecular NOE (solid grey arrows), intramolecular NOE (solid black arrows) and exchange (dashed grey arrow) pathways for $[\text{Ch}]^+[\text{OAc}]^-/\text{H}_2\text{O}$ mixture, stemming from the 1D and 2D NMR measurements. Dotted lines indicate H-bonds. Pathways from the other methyl/methylene groups have been omitted for clarity.

that stabilize the aggregation of the IL/water mixture. The position of the anion is consistent with the minimum energy location calculated by Shaukat et al. [105].

4. Conclusions

The dynamics of choline acetate $[\text{Ch}]^+[\text{OAc}]^-$ and choline trifluoroacetate $[\text{Ch}]^+[\text{TFA}]^-$ mixtures with 30 wt% water have been studied by variable temperature ^1H and ^{19}F NMR. Compared to bulk water, the ^1H chemical shift change of H_2O was lower for the $[\text{Ch}]^+[\text{TFA}]^-$ than for the $[\text{Ch}]^+[\text{OAc}]^-$ mixture, which is attributed to the higher acidity and therefore lower H-bond activity of trifluoroacetate. In addition, a strong temperature dependent effect is observed for the linewidth of the H_2O proton resonance, which is representative for chemical exchange processes between H_2O and $-\text{OH}$. Rotational correlation times were separately obtained for the cation, anion and water. The acetate/trifluoroacetate anions, the choline cations and the H_2O molecules displayed similar rotational correlation times, which showed that a significant fraction of the species in the mixture exhibit collective reorientation even at room temperatures. Thereby, the difference between the cation and the anion was larger than between the cation and the water, yet variable temperature 2D and 1D NOESY/ROESY experiments showed that intermolecular correlations between the cation and anion are also still present at 306 K.

At low temperatures strong negative intermolecular NOEs were observed between choline, acetate and water protons, originating from a stable H-bonding state. The similarity in cross-relaxation rates between choline, acetate and water as well as the difference in the cationic and anionic translational diffusion coefficients points towards a formation of solvent-shared ion pairs (SIP) and an accompanying association of the species that influences physicochemical properties such as viscosity, melting point and surface tension. The independent long-range motion of cations and anions enables charge transport, which is a necessary prerequisite for the suitability of these mixtures in electrochemical applications.

When analyzed using an Arrhenius relation, temperature dependent relaxation rates show an increasing energy of activation with decreasing temperature. The high-temperature values are similar to figures typically found for molecular liquids, while the values below the freezing point of pure water show a significantly increased entropy contribution. In combination with relaxation data, this points at a change of the main relaxation-affecting dynamic process from molecular rotation at room temperature to pseudorotation at low temperature, with a relatively static local structure of cations and H₂O and, to a lesser extent, also anions, where relaxation is induced by a rearrangement of the H-bond network. In addition, the combination of data from the different experiments hint that these ILs behave similarly as a DES, with water as the Lewis acid.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2020.114934>.

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