The influence of deuterium isotope effects on structural rearrangements, ensemble equilibria, and hydrogen bonding in protic ionic liquids

Alexander E. Khudozhitkov[a,b], Peter Stange[c], Dietmar Paschek[c], Alexander G. Stepanov[a], Daniil I. Kolokolov[a,b]*, Ralf Ludwig[c,d]*

a Boreskov Institute of Catalysis, Siberian Branch of Russian Academy of Sciences, Prospekt Akademika Lavrentieva 5, Novosibirsk 630090, Russia; E-mail: kdi@catalysis.ru

b Novosibirsk State University, Pirogova Street 2, Novosibirsk 630090, Russia

c Universität Rostock, Institut für Chemie, Abteilung für Physikalische Chemie, Albert-Einstein-Straße 27, 18059 Rostock, Germany; Tel: 49 381 498 6517; E-mail: ralf.ludwig@uni-rostock.de

d Leibniz-Institut für Katalyse an der Universität Rostock e.V., Albert-Einstein-Str. 29a, 18059 Rostock (Germany)

Abstract

We report strong isotope effects for the protic ionic liquid triethylammonium methanesulfonate [TEA][OMs] by means of deuterium solid-state NMR spectroscopy covering broad temperature ranges from 65 K to 313 K. Both isotopically labelled PILs differ in non-deuterated and fully deuterated ethyl groups of the triethyl ammonium cations. The N-D bond of both cations is used as sensitive probe for hydrogen bonding and structural ordering. The ^{2}H NMR line shape analysis provides the deuteron quadrupole coupling constants and the characteristics of a broad heterogeneous phase with simultaneously present static and mobile states indicating plastic crystal behavior. The temperatures where both states are equally populated differ by about 80 K for the two PILs, showing that deuteration of the ethyl groups in the trialkylammonium cations tremendously shifts the equilibrium towards the static state. In addition, it leads to a significant less cooperative transition, associated with a significantly reduced standard molar transition entropy.

Isotope effects play a pivotal role in chemistry and biology.[1] Protein stability strongly depends on deuteration of the protein-backbone or deuteration of the solvent water. The change from protonated to deuterated water increases the strength of the solvent-solvent as well as the solvent-protein hydrogen bonds and thus significantly influences the protein-folding process.[2] Isotope effects are also crucial in atmospheric chemistry, where isotopic compositions change as a function of temperature and pressure, strongly affecting chemical reactions.[3] D-bonds are assumed to be stronger than H-bonds due to quantum effects, mainly the lowering of the zero point vibrational energy. Since H and D are electronically identical, the total energies of the related complexes are equal, and differences are associated with the masses and mass distributions, primarily governed by vibrational energies. What is well established for hydrogen-bonded molecular liquids such as water and methanol is still unclear for hydrogen bonded cations and anions in ionic liquids (ILs).[4] These liquid materials attract increasing interest in science and technology due to their unique properties, which result from the delicate balance of Coulomb interactions, hydrogen bonding and dispersion forces between the charged entities.[5] Specific strength, locality and directionality of the different types of interactions govern the structure, dynamics, and phase behavior of ILs.[6] For structure determination of molecular as well as ionic liquids, isotopic labeling is used in neutron diffraction experiments assuming that the structure is similar for the differently labelled species, regardless where and to which extend they are deuterated. However, there are some scattering studies indicating that this prerequisite is not always justified.[4]

The importance of high conductivity electrolytes for devices such as fuel cells, batteries, and solar cells is a compelling motivation for studying deuterium isotope effects in ILs.[7] It is the purpose of our work to study the influences of isotopic substitution on hydrogen bonding and structural ordering of the model protic ionic liquid (PIL) triethylammonium methanesulfonate [TEA][OMs] by means of deuterium solid-state NMR spectroscopy. We use the N-D deuterons of the triethylammonium cations for probing structural rearrangements, equilibria between static and mobile states and hydrogen bonding depending on selective deuteration of the three ethyl groups. We show that structural changes and interactions vary characteristically with temperature and that the equilibria between static and mobile fractions in the PIL are highly sensitive to deuteration of the alkane chains with respect to both, the transition temperature and the cooperativity of the transition. We demonstrate that solid-state NMR spectroscopy is a suitable method for understanding the origin of changes in thermodynamic, structural and dynamical properties in complex materials caused by isotopic substitution.

We synthesized the PILs triethylammonium methanesulfonate [(CH$_3$CH$_2$)$_3$NH][SO$_3$CH$_3$] ([TEA-d$_0$][OMs]) and [(CD$_3$CD$_2$)$_3$NH][SO$_3$CH$_3$] ([TEA-d$_{15}$][OMs]) according to the previously reported and here improved procedure (see Supporting Information (SI)).[6c, 8] Hydrogen/deuterium (H/D) exchange was achieved by mixing the PILs with D$_2$O and removing water several times until nearly 100% deuteration was reached as proven by ^{1}H NMR. The resulting PILs ([TEA-d$_1$][OMs]) and ([TEA-d$_{16}$][OMs]) have been dried under vacuum (at $3 \cdot 10^{-3}$ mbar) for several days and the final water concentration (< 15 ppm) has been checked by Karl-Fischer titration. The PILs were then loaded into 5 mm glass tubes, properly degassed by bubbling through nitrogen, sealed off and finally transferred into an NMR probe for analysis with ^{2}H NMR spectroscopy.

^{2}H NMR experiments were performed at the Larmor frequency $\omega_0/2\pi = 61.424$ MHz on a Bruker Avance-400 spectrometer using a high-power probe with a 5 mm horizontal solenoid coil. All ^{2}H NMR spectra were obtained by a Fourier transform of a quadrature-detected and phase-cycled quadrupole echo after two phase-alternating 90°-pulses in the pulse sequence ($90°_x - \tau - 90°_y - \tau - $ acquisition$ - t$), where $\tau = 20$ μs and t is a repetition time of the sequence during accumulation of the NMR signal. The duration of $\pi/2$ pulse was 1.8-1.9 μs. Spectra were typically obtained with 400−2000 scans at low temperature and 40-80 scans at high temperature with a repetition time ranging from 0.2 to 3 s.

We recorded the ^{2}H NMR spectra for a broad temperature range between 67 and 316 K. In **Fig. 1** we show the measured, the simulated and the deconvoluted Pake-like spectra at 113 K and 143 K for the PIL [TEA-d$_{16}$][OMs] (see **Scheme 1**). The ^{2}H spectra are a superposition of three Pake-doublets with DQCCs for the methyl deuterons (Q$_{CD3}$= 52 kHz), the methylene deuterons (Q$_{CD2}$= 170 kHz) and the ND deuteron (Q$_{ND}$= 147 kHz).[9] The measured DQCC for C-D in the methylene group of about 170 kHz is typical for sp^3 hybridized deuterocarbons and obviously describes the static pattern well.[10] Usually the nuclear contribution to the electric field gradient decreases in the series sp, sp^2 and sp^3. However, the extremely small value for the methyl deuterons of about 52 kHz indicates significant motional narrowing which is expected from fast methyl group rotation still present at low temperatures.[11] Thus this value is similar to that of the fast reorienting methyl group in toluene-d$_3$ for temperatures below T_g,[12] or n-dodecane-d$_3$ below melting point.[13]

The temperature dependent DQCCs for all C-D fragments are given in the SI. Here we would like to focus on the DQCCs of the N-D deuteron in the PIL [TEA-d$_{16}$][OMs] compared to those in PIL [TEA-d$_1$][OMs], differing in isotopical labelling of the ethylene groups. The DQCC of

the N-D deuterons is determined by the magnitude of the electric field gradient (*efg*) at the position of the nucleus. This *efg* originates mainly from the electrons of N-D group that participates in hydrogen bonding (N-D···O). It has been shown for molecular liquids that the DQCC is a sensitive probe for hydrogen bonding. For water, DQCC values decrease from the gas phase (308 kHz) via the liquid phase (~254 kHz) down to the ice value (214 kHz) due to increasing HB strength in this order.[14]

The N-D DQCCs of both PILs are shown in **Fig. 2** as a function of temperature between 67 K and 313 K. We clearly observe that the electric field gradient tensor at the nuclei of the N-D deuterons changes. Qualitatively, the behaviour is similar for the ND fragment in both PILs, [TEA-d_1][OMs] and [TEA-d_{16}][OMs]. First, we observe the real DQCC Q_0 of about 147 kHz at 67 K. Since its value remains unchanged for T < 103 K, we can conclude that it is the value not averaged by bond librations.[15]

Overall, the DQCC of [TEA-d_{16}][OMs] is significantly smaller than those of [TEA-d_1][OMs] (149 kHz at 143 K) and [TEA-d_1][NTf$_2$] (161 kHz at 143 K).[16] The reason is Coulomb-enhanced hydrogen bonding of the [TEA] cation with the strongest interacting anion [OMs]. Upon heating, the effective DQCCs Q_{eff} decrease due to increasing amplitude of the librations of the ND bond direction.[17] At certain temperatures, this process reaches a maximum of its efficiency and is followed by an increase of Q_{eff} towards a new stabilisation value Q_S, which is significantly below the non-averaged Q_0 value at lowest temperature.

Our data suggest that the ND deuterons are sensitive probes not only for hydrogen bonding between cation and anion, but are also indicating different interaction strength and structural rearrangements in the two PILs affected by different isotopic labelling. The DQCCs of the PIL with the fully deuterated [TEA-d_{16}] cation describe a similar but narrower temperature profile. The almost identical temperature profile is imaged within about ΔT=150 K for [TEA-d_{16}][OMs] compared to about ΔT=250 K for [TEA-d_1][OMs]. The non-averaged static Q_0 is higher and reached at much higher temperatures compared to the case when only the ND group is deuterated. The lowest value of the effective Q_{eff} is consequently higher too, and is reached by about 50 K *below* the similar minimum for the partially deuterated cation.

Finally, the stabilization value Q_s is roughly the same, which explains, why in the melted state there are no differences in dynamics. Thus, despite the difference in the DQCC value is always within +5 kHz, we can conclude, that the fully isotope substitution of the PIL's cation notably alters the EFG tensor on the ND fragment of the cation. Since the latter is strongly hydrogen bonded with the anions, we can speculate, that the full deuteration is decreasing the hydrogen

bond strength. To our knowledge, this is the first experimental evidence on the isotope effect on the hydrogen bonding in PILs due to H/D exchange not involving the N-H proton.

In particular, we focus on DQCCs of PILs [TEA-d_1][OMs] and [TEA-d_{16}][OMs] for temperatures at 113 K and 143 K, where both PILs show the same DQCCs of about 140 kHz. As shown in **Fig. 3**, the deconvoluted Pake patterns for the N-D deuterons is similar, indicating the same H-bond strength at about 30 K different temperatures. Apparently, the same HB strength is present for [TEA-d_{16}][OMs] already at higher temperature. Such a temperature difference between differently isotopically labelled compounds has been observed of molecular liquid such as water and alcohols from high energy photon diffraction experiments.[4a-c]

While the DQCCs are sensitive to changes present within a single cation-anion pair, we are also interested to see how isotopic substitution affects the behavior of the whole pair in the solid region. For that purpose, we addressed the dynamically heterogeneous phase being a remarkable feature of the PIL [TEA-d_1][OMs] in the temperature range between 220 K and 300 K. This coincides with the differential scanning calorimetry (DSC) traces of [TEA-d_1][OMs] as observed upon heating and cooling. We observed the melting peak at 306 K and a cold crystallization peak at 240 K.[17] The ^{2}H spectra measured between the melting and the crystallisation temperatures can be simulated by the superposition of both line shapes.

Typical ^{2}H spectra recorded at 233 K are shown in **Fig. 4**, exhibiting a Pake patterns and a small narrow line simultaneously.[16-17] The ^{2}H NMR patterns of the high temperature solid phase showed that part of the molecules are still rigidly bound in ground state *I* (also denoted as static state), while others are found in a highly mobile state *II* (also denoted as mobile state). From the analysis of the ^{2}H NMR spectra line shape we can deduce thermodynamic properties characterizing the transition from the rigid to the mobile state of the PIL.[18] The relative populations of the rigid [TEA]$^+$ cations p_{static} and the mobile fraction p_{mobile} are proportional to the relative intensities of anisotropic and isotropic components of ^{2}H NMR spectrum, respectively. The calculated isotropic and anisotropic fractions of the ^{2}H spectra for the two samples [TEA-d_1][OMs] and [TEA-d_{16}][OMs] are shown in **Fig. 5a**. It is evident, that the equilibrium in case of the fully deuterated cations is strongly shifted toward the static state *I*. The temperatures where the static and mobile fractions are equally populated at about 236 K for [TEA-d_1][OMs] compared to predicted 316 K for [TEA-d_{16}][OMs]. Thus, there is a 80 K difference with a preference for the ethyl-deuterated species, suggesting an enormous isotope effect.

Thus, the present PILs can be regarded as plastic crystals exhibiting states of coupling intermediate between static and mobile units, with a definite three-dimensional lattice, but with rotational motion of the same fraction of the species possible. They have long-range order but short-range disorder, which typically originates from rotational motions of the molecular ions, already present in the solid phases. It has been shown earlier that mainly the cation is determining plasticity of an ionic liquid.[19]

The mobile/static equilibrium is described by the equilibrium constant $K_{eq}=p_{mobile}/p_{static}$ as a function of temperature. Here p_{mobile} and p_{static} represent the corresponding populations and are shown in **Fig. 5a**. Note that temperature region associated with the transition is centered around 236 K for [TEA-d_1][OMs] and about 316 K for [TEA-d_{16}][OMs], which represents an astonishing 80 K shift in temperature due to the deuteration of the alkane chains. As mentioned earlier, a visual inspection of both transitions in **Fig. 5a** is also suggesting that the transition for [TEA-d_{16}][OMs] is extending over a broader temperature range than for [TEA-d_1][OMs]. The molar standard Gibbs free energy difference $\Delta G^o(T) = -RT \ln K_{eq}$ associated with the coexistence of both states obviously has to be temperature dependent for describing such a transition. In the simplest scenario (denoted as the "van 't Hoff scenario") the temperature dependence of $\Delta G^o(T)$ could be expressed by temperature independent molar standard transition enthalpies and entropies with $\Delta G^o(T) = \Delta H^o - T \Delta S^o$. In such a case, the data in the van 't Hoff plot shown in **Fig. 5b** should follow a strictly linear behaviour. Since this condition is not perfectly fulfilled, we also consider a second order expansion of the molar standard Gibbs free energy difference according to[20]

$$\Delta G^o(T) = \Delta S^o_{T_t}(T_t - T) - \Delta C_p \left[T \left(\ln \left(\frac{T}{T_t} \right) - 1 \right) + T_t \right] \tag{1}$$

Here T_t represents the transition temperature, where the condition $p_{mobile}/p_{static} = 1$ is fulfilled, $\Delta S^o_{T_t}$ is the molar standard entropy difference at the transition temperature T_t, and ΔC_p indicates the heat capacity difference between the two states. Fitted parameters for both scenarios are summarized in **Table I**. We would like to point out that it is maybe not surprising that the condition $\Delta C_p = 0$ is not perfectly fulfilled, since we still deal with a material involving many degrees of freedom, and both states are likely to be consisting of a broad variety of conformational states. Such a behaviour is not uncommon in soft condensed matter and can be found in order/disorder transitions where many degrees of freedom are involved, such the temperature induced unfolding of globular proteins.[20,21] The fact that we deal with a broad

6

temperature transition between the mobile and static states, indicates that this transition should not regarded as a phase transition, but instead as a transition between two conformational ensembles confined to rather localized domains. If the "communication" between these local domains is effectively suppressed, a phase transition is prevented and we end up with the observed "uncooperative" form of transition. A simple example for such a localized order/disorder transition, albeit from a different realm of soft condensed matter science, would be the extensively studied helix/coil transition of helical peptide chains where the "sharpness" (i.e. inverse temperature range) of the transition increases with the length of the peptide chains (i.e. the domain-size).[22,23] Here the size of the molar standard transition entropy (which scales linearly with the peptide chain length) determines the "cooperativity" of the transition. In the present case a similar behaviour is observed: In both scenarios the entropy differences ΔS^o and $\Delta S^o_{T_t}$ are significantly smaller for [TEA-d$_{16}$][OMs] than for [TEA-d$_1$][OMs], which is in line with an observation of less "cooperative" transition, leading to a broader transition temperature range for [TEA-d$_{16}$][OMs]. The location of the transition temperature is depending on the balance between the molar standard entropy and enthalpy differences, and is determined by larger relative decrease in ΔS^o with respect to ΔH^o, when exchanging the cation [TEA-d$_1$] by [TEA-d$_{16}$]. A noteworthy observation is the different sign of ΔC_p found for [TEA-d$_1$][OMs] and [TEA-d$_{16}$][OMs], which is reflecting the different curvatures the [TEA-d$_1$][OMs] and [TEA-d$_{16}$][OMs] data in the van 't Hoff Plot shown in **Fig. 5b**. Finally, we would like to emphasize that our data represent to our knowledge the first observation of an isotope effect on the ion pair mobility in frozen ionic liquids reported so far.

In present work, we report strong isotope effects for the protic ionic liquid triethylammonium methanesulfonate [TEA][OMs] by means of deuteron solid-state NMR spectroscopy. We used the N-D bond of both cations as sensitive probe for hydrogen bonding and structural ordering. The isotopically labelled PILs [TEA-d$_1$][OMs] and [TEA-d$_{16}$][OMs] differ in non-deuterated and fully deuterated ethyl groups of the triethyammonium cations. The ^{2}H NMR line shape analysis provides the quadrupole coupling constants for the deuterons in the CD$_3$, CD$_2$ and ND fragments. The ND spectra measured over a broad temperature range from 65 K to 313 K showed a characteristic broad heterogeneous phase with simultaneously present static and mobile states indicating plastic crystal behavior. The temperatures where both states in the two PILs are equally populated differ by about 80 K showing that deuteration of the ethyl groups in the trialkylammonium cations can tremendously shift the equilibrium

towards the static state. Apparently, the PIL [TEA-d$_{16}$][OMs] is more structured than [TEA-d$_1$][OMs] at similar temperatures. The broad transition temperature between the static and mobile states should be regarded as a transition between two conformational ensembles confined to rather localized domains. A careful thermodynamic analysis shows that the static/mobile transition is governed by the entropy differences which are smaller for [TEA-d$_{16}$][OMs] than for [TEA-d$_1$][OMs], finally leading to a broader transition temperature range for the first. This study underlines the relevance of isotope effects on hydrogen bonding, structural arrangements and ensemble equilibria in protic ionic liquids.

References

[1] H.-H. Limbach, G. S. Denisov, N. S. Golubev, *Isotope Effects in the Biological and Chemical Sciences*, CRC Press, Boca Raton, **2005**.

[2] P. M. J., A. R. Clarke, *Biochemistry* **1997**, *36*, 5786-5794.

[3] C. A. M. Brenninkmeijer, C. Janssen, J. Kaiser, T. Röckmann, T. S. Rhee, S. S. Assonov, *Chem. Rev.* **2003**, *103*, 5125-5162.

[4] a)C. J. Benmore, P. A. Egelstaff, *J. Phys.: Condens. Matter* **1996**, *8*, 9429-9432; b)B. Tomberli, C. J. Benmore, P. A. Egelstaff, J. Neuefeind, V. Honkimäki, *J. Phys.: Condens. Matter* **2000**, *12*, 2597-2612; c)B. Tomberli, C. J. Benmore, P. A. Egelstaff, J. Neuefeind, V. Honkimäki, *Europhys. Lett.* **2001**, *55*, 341-347; d)S. Scheiner, M. Čuma, *J. Am. Chem. Soc.* **1996**, *118*, 1511-1521; e)T. Driesner, *Science* **1997**, *277*, 791-794; f)R. Ludwig, *ChemPhysChem* **2005**, *6*, 1369-1375.

[5] a)P. Wasserscheid, T. I. L. i. S. Welton, *Ionic Liquids in Synthesis*, 2nd ed. Wiley-VCH ed., Weinheim, **2008**; b)T. Welton, *Chem. Rev.* **1999**, *99*, 2071-2084; c)N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123-150.

[6] a)K. Fumino, S. Reimann, R. Ludwig, *Phys. Chem. Chem. Phys.* **2014**, *16*, 21903-21929; b)P. A. Hunt, C. R. Ashworth, R. P. Matthews, *Chem. Soc. Rev.* **2015**, *44*, 1257-1288; c)K. Fumino, V. Fossog, P. Stange, D. Paschek, R. Hempelmann, R. Ludwig, *Angew. Chem., Int. Ed.* **2015**, *54*, 2792-2795.

[7] a)S. P. M. Ventura, F. A. e Silva, M. V. Quental, D. Mondal, M. G. Freire, J. A. P. Coutinho, *Chem. Rev.* **2017**, *117*, 6984-7052; b)M. Galiński, A. Lewandowski, I. Stępniak, *Electrochim. Acta* **2006**, *51*, 5567-5580; c)S. Menne, J. Pires, M. Anouti, A. Balducci, *Electrochem. Commun.* **2013**, *31*, 39–41.

[8]   K. Fumino, V. Fossog, K. Wittler, R. Hempelmann, R. Ludwig, *Angew. Chem., Int. Ed.* **2013**, *52*, 2368-2372.

[9]   a)G. E. Pake, *J. Chem. Phys.* **1948**, *16*, 327-336; b)A. Abragam, *The Principles of Nuclear Magnetism*, Oxford University Press, Oxford, UK, **1961**.

[10]   P. L. Olympia, I. Y. Wei, B. M. Fung, *J. Chem. Phys.* **1969**, *51*, 1610-1614.

[11]   M. Flämig, M. Becher, M. Hofmann, T. Körber, B. Kresse, A. F. Privalov, L. Willner, D. Kruk, F. Fujara, E. A. Rössler, *J. Phys. Chem. B.* **2016**, *120*, 7754-7766.

[12]   E. Rössler, H. Sillescu, *Chem. Phys. Lett.* **1984**, *112*, 94-98.

[13]   D. I. Kolokolov, S. S. Arzumanov, A. G. Stepanov, H. Jobic, *J. Phys. Chem. C* **2007**, *111*, 4393−4403.

[14]   a)H. Bluyssen, J. Verhoeven, A. Dymanus, *Phys. Lett. A* **1967**, *25*, 214-215; b)D. T. Edmonds, A. L. Mackay, *J. Magn. Reson.* **1975**, *20*, 515-519; c)R. Eggenberger, S. Gerber, H. Huber, D. Searles, M. Welker, *J. Chem. Phys.* **1992**, *97*, 5898-5904.

[15]   a)D. T. Amm, S. L. Segel, T. J. Bastow, K. R. Jeffrey, *Z. Naturforsch.* **1986**, *41a*, 305-310; b)D. I. Kolokolov, A. G. Stepanov, H. Jobic, *J. Phys. Chem. C* **2015**, *119*, 27512-27520.

[16]   A. E. Khudozhitkov, P. Stange, A. M. Bonsa, V. Overbeck, A. Appelhagen, A. G. Stepanov, D. I. Kolokolov, D. Paschek, R. Ludwig, *Chem. Commun.* **2018**, *54*, 3098-3101.

[17]   A. E. Khudozhitkov, V. Overbeck, P. Stange, A. Strate, D. Zaitsau, A. Appelhagen, D. Michalik, A. G. Stepanov, D. I. Kolokolov, D. Paschek, R. Ludwig, *Phys. Chem. Chem. Phys.* **2019**, *21*, 25597-25605.

[18]   A. E. Khudozhitkov, P. Stange, A. G. Stepanov, D. I. Kolokolov, R. Ludwig, *Phys Chem Chem Phys* **2022**, *24*, 6064-6071.

[19]   J. M. Pringle, P. C. Howlett, D. R. MacFarlane, M. Forsyth, *J. Mater. Chem.* **2010**, *20*, 2056-2062.

[20]   D. Paschek, S. Hempel, A. E. García. *Proc. Natl. Acad. Sci. USA* **2008**, 105, 17754-17759.

[21]   G. I. Makhatadze, P. L. Privalov. *Adv. Protein Chem.* **1995**, 47, 307–425.

[22]   B. H. Zimm, J. K. Bragg. *J. Chem. Phys.* **1959**, 31, 526–535.

[23]   S. Lifson, A. Roig. *J. Chem. Phys.*, **1961**, 34, 1963–1974.
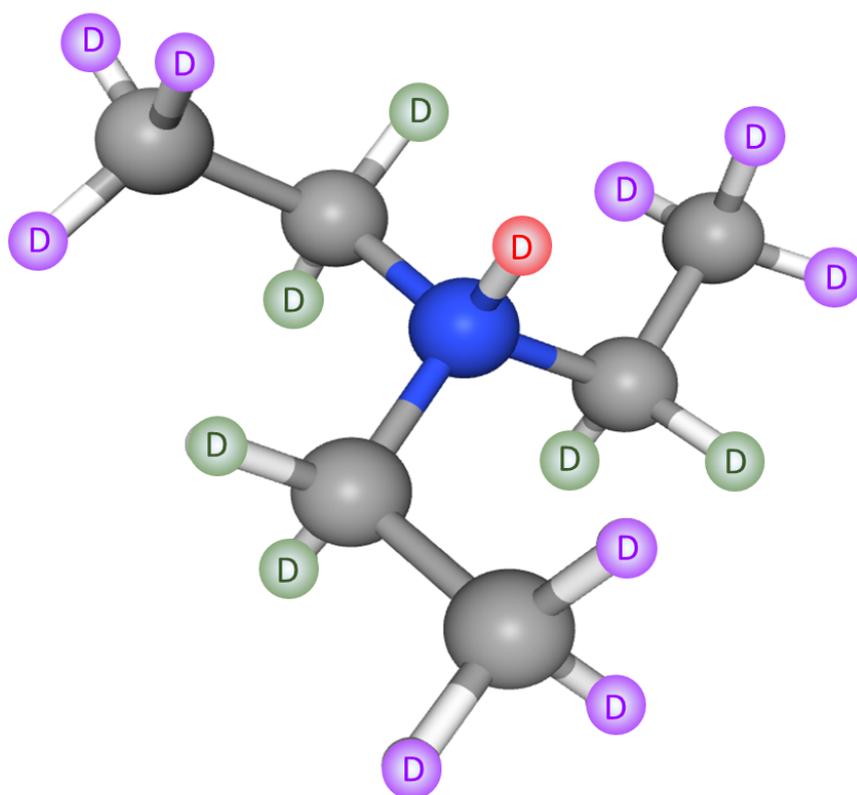
Scheme 1: Fully deuterated triethylammonium cation [TEA-d$_{16}$][OMs] in the protic ionic liquid [(CD$_3$CD$_2$)$_3$ND][SO$_3$CH$_3$] indicating the colour code used for the different deuterons in the amide ND (red), the methylene CD$_2$ (green) and the methyl CD$_3$ (violet) groups.
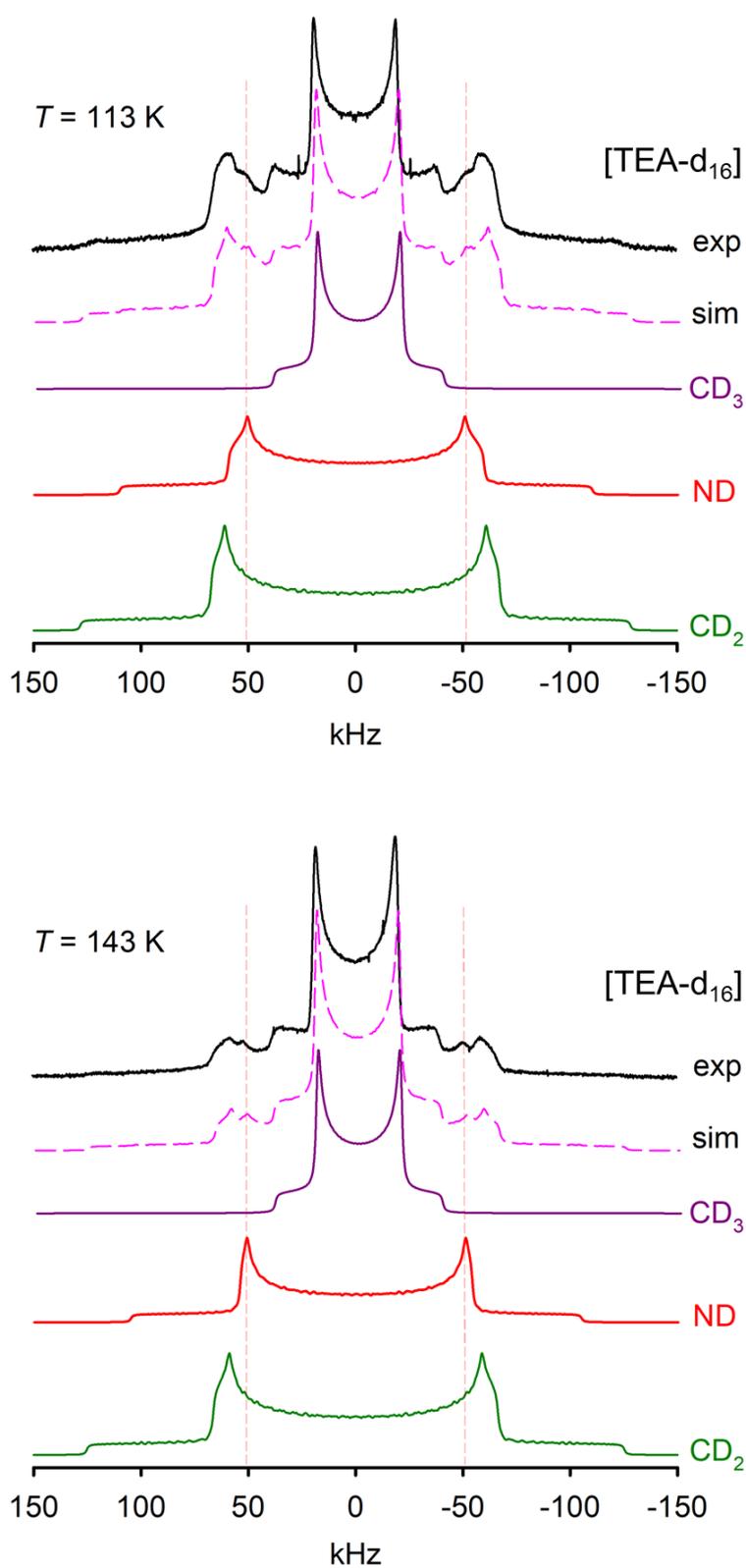
Figure 1. ^{2}H NMR spectrum of [TEA-d$_{16}$][OMs] at T= 113 K and T=143 K: For both temperatures we show the experimental (exp), simulated (sim) and deconvoluted spectra for the deuterons the amide ND (red), the methylene CD$_2$ (green) and the methyl CD$_3$ (violet) groups.
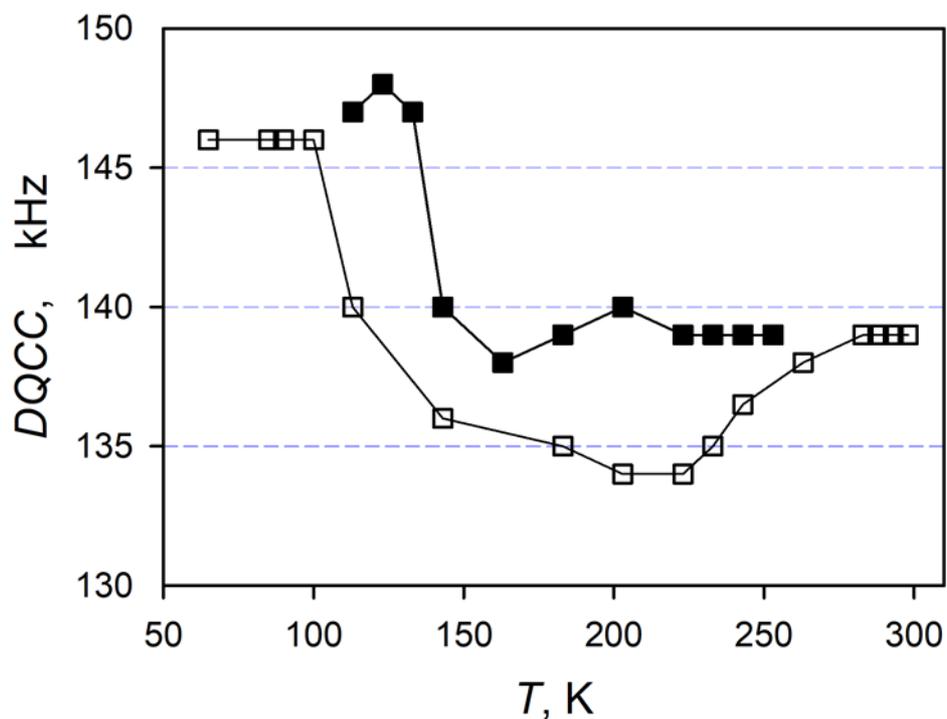
Figure 2. DQCCs observed in the ^{2}H solid-state NMR patterns of PILs [TEA-d$_1$][OMs] (open squares) and [TEA-d$_{16}$][OMs] (filled squares) as a function of temperature between 65 K and 313 K. A particular focus is put on the DQCCs at T=113 K and T=143 K as discussed in the text.
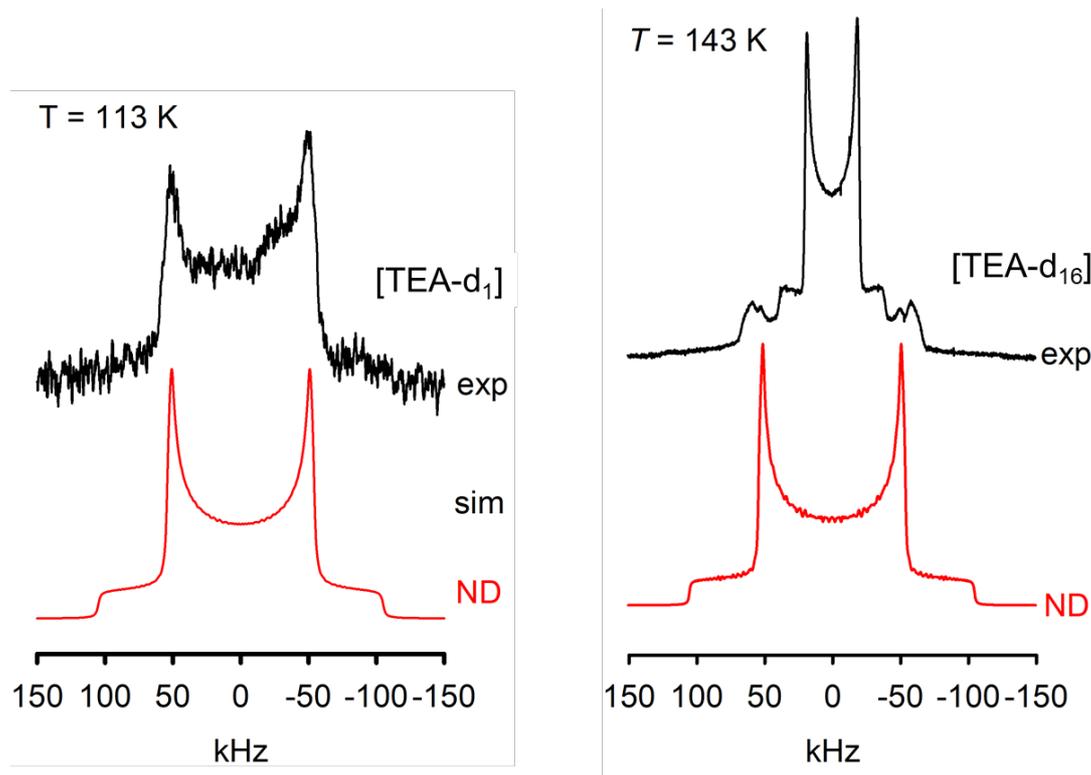
Figure 3. Measured and deconvoluted ^{2}H solid-state NMR patterns for the N-D deuterons of PIL [TEA-d$_1$][OMs] at 113 K (left) and [TEA-d$_{16}$][OMs] at 143 K (right). The deconvoluted line shapes are similar und exhibit the same DQCCs of about 140 kHz.
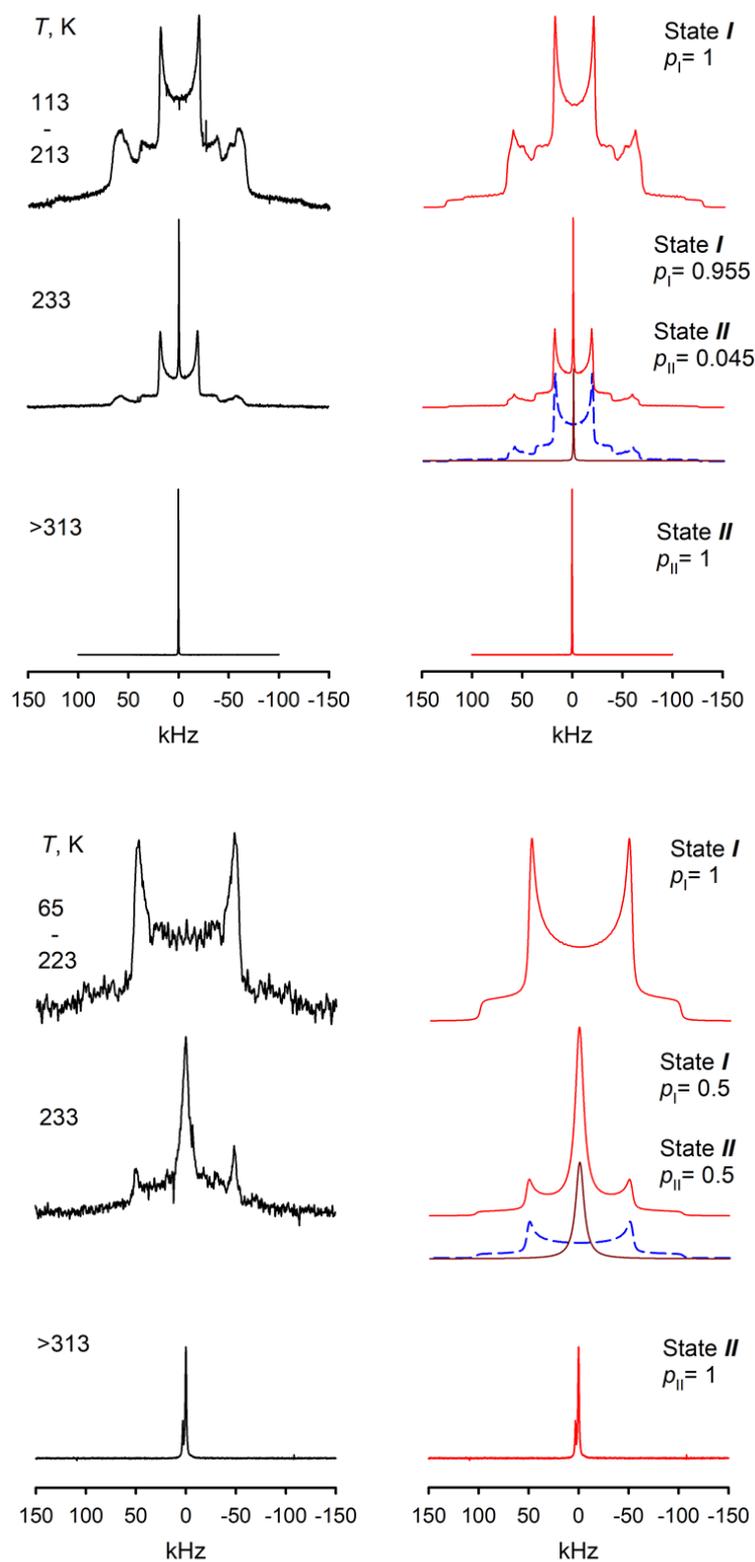
Figure 4. The ^2H NMR spectra of PILs [TEA-d_{16}][OMs] (top) and [TEA-d_1][OMs] (bottom) for different temperature ranges showing the static patterns, the heterogeneous phase with both, the mobile and the static states and the pure mobile contribution.
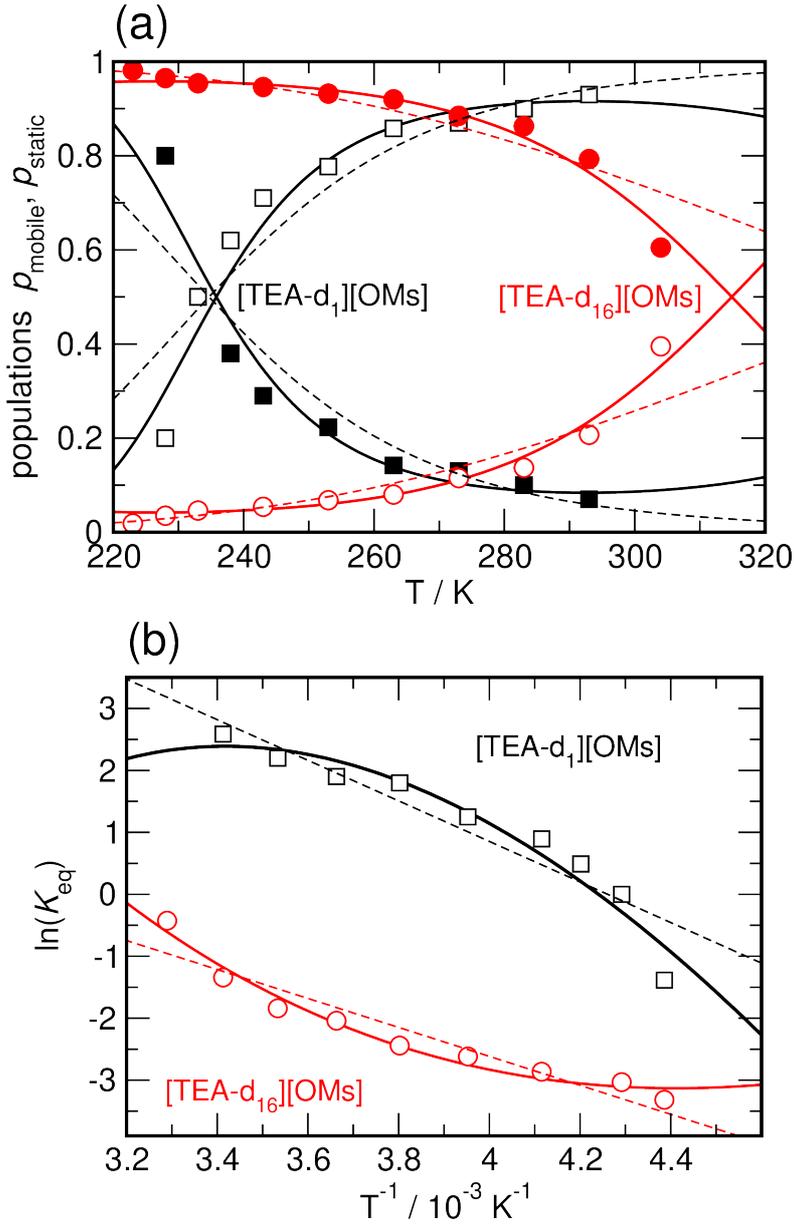
Figure 5: Thermodynamic analysis of the mobile/static transition observed in [TEA-d$_1$][OMs] and [TEA-d$_{16}$][OMs]. Solid lines: fit to a second order expansion of the molar standard Gibbs free energy $\Delta G^o = -RT \ln K_{eq}$ with $K_{eq}=p_{mobile}/p_{static}$ using $\Delta G^o(T) = \Delta S^o_{T_t}(T_t - T) - \Delta C_p \left[T \left(\ln \left(\frac{T}{T_t} \right) - 1 \right) + T_t \right]$. Dashed lines: fit to the corresponding first order expansion of $\Delta G^o(T)$ using $\Delta C_p = 0$, also called van 't Hoff analysis. The fitted parameters are summarized in **Table 1**. (a) Population of the static (filled symbols) and mobile (open symbols) states p_{static} and p_{mobile} for [TEA-d$_1$][OMs] (shown in black) and [TEA-d$_{16}$][OMs] (shown in red). (b) van 't Hoff plot of the logarithm of the equilibrium constant K_{eq} vs. the inverse temperature.

	[TEA-d$_1$][OMs]	[TEA-d$_{16}$][OMs]
van 't Hoff analysis (ΔC_p=0):		
ΔS°/J K^{-1}mol^{-1}	116	56
ΔH°/kJ mol^{-1}	27.2	19.4
second order expansion ($\Delta C_p \neq 0$):		
$\Delta S^{\circ}_{T_t}$/J K^{-1}mol^{-1}	191	150
ΔC_p/J K^{-1}mol^{-1}	-793	535
ΔT_t/K	235.8	314.9

Table 1: Thermodynamic parameters describing the mobile/static transition observed in [TEA-d$_1$][OMs] and [TEA-d$_{16}$][OMs] using first and second order expansions of the molar standard Gibbs free energy difference according to $\Delta G^{\circ} = -\text{RT} \ln K_{\text{eq}}$.