

Supporting Information: Deuteron Quadrupole Coupling Constants and Reorientational Correlation Times in Protic Ionic Liquids by Means of NMR Relaxation Time Experiments, DFT-Calculations and Molecular Dynamics Simulations

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1 Molecular Dynamics Simulations

To complement the NMR experiments, we compute the reorientational dynamics of the Triethylammonium (TEA) cation in three different protic ionic liquids (Triethylammonium-Methylsulfonate, Triethylammonium-Triflate, Triethylammonium-Bis(Trifluoromethyl-Sulfonyl)Imide) from MD simulation data. We are using recently introduced all-atom forcefield models [1, 2], and are covering the temperature range between 300 K and 400 K, while employing simulation length up to 100 ns. The employed forcefield parameters for TEA, Methylsulfonate (MS), and Triflate (TF) are available from Ref. [1], whereas the parameters for the Bis(Trifluoromethyl-Sulfonyl)Imide-anion (NTf₂) were taken from Ref. [2].

All simulated protic ionic liquids are presented by systems composed of 256 ion pairs in a cubic simulation box using periodic boundary conditions. All molecular dynamics (MD) simulations are performed in the isobaric isothermal (*NPT*) ensemble, employing Nosé-Hoover thermostats [3, 4], and Rahman-Parrinello barostats [5, 6], using coupling-times of $\tau_T = 0.5$ ps, and $\tau_p = 2$ ps, respectively. The electrostatic interactions are treated in the “full potential” approach by the smooth particle mesh Ewald summation [7] with a real space cutoff of 1.0 nm and a mesh spacing of approximately 0.12 nm and 4th order interpolation. The Ewald convergence factor α was set to 3.38 nm^{-1} (corresponding to a relative accuracy of the Ewald sum of 10^{-5}).

A 2.0 fs timestep was used for all simulations and the constraints were solved using the SETTLE procedure [8]. During the simulations all bond-length were kept fixed. All simulations reported here were carried out using the GROMACS 5 program [9, 10]. For all reported mixtures and temperatures initial equilibration runs of 1 ns length were performed using the Berendsen weak coupling scheme for pressure and temperature control $\tau_T = \tau_p = 0.5$ ps [11]. Production

runs of 100 ns (300 K), 48 ns (320 K, 340 K, 360 K, 380 K), and 24 ns (400 K) simulation-length were finally recorded and analyzed. All simulations are carried out at a pressure of 1 bar.

2 Reorientational Dynamics

We determine the reorientational dynamics of the TEA cation by focusing the time evolution of the orientation of N-D vector in an external laboratory frame. The time-correlation function $C(t)$ of the second Legendre polynomial of the angle θ of the N-D vector with a fixed external axis of reference $P_2\{\cos[\theta]\} = \{3\cos^2[\theta] - 1\}/2$ is computed according to

$$C(t) = \langle P_2\{\cos[\theta(0)]\} \cdot P_2\{\cos[\theta(t)]\} \rangle. \quad (1)$$

Assuming that the electric field gradient (EFG) at the deuteron position of the N-D bond is solely determined by the surrounding electron distribution and does not depend on the local molecular environment, as well as the actual molecular conformation of the TEA-cation, and assuming that the reorientational motion is fast on the NMR timescale, the relaxation rate is directly proportional to the quadrupole coupling constant times the reorientational correlation time of the N-D bond τ_c with

$$\left(\frac{1}{T_1}\right)_D = \frac{3}{2}\pi^2 \left(1 + \frac{\eta_D^2}{3}\right) \chi_D^2 \cdot \tau_c. \quad (2)$$

For the case of the extreme narrowing limit, the correlation time τ_c corresponds to an integral over the correlation function $C(t)$ with

$$\tau_c = \int_0^{\infty} C(t) dt. \quad (3)$$

For estimating τ_c , the long-time behavior of $C(t)$ needs to be properly accounted for. To achieve this, we fitted the time correlation function $C(t)$ to a combined mono-exponential and stretched exponential representation following

$$C(t) = A_1 \cdot e^{-(t/\tau_1)^{\beta_1}} + A_2 \cdot e^{-t/\tau_2}, \quad (4)$$

leading to the following expression for the integrated correlation time [12]:

$$\tau_c = A_1 \cdot \frac{\tau_1}{\beta_1} \Gamma(\beta_1^{-1}) + A_2 \cdot \tau_2 \quad (5)$$

Here $\Gamma(\dots)$ is representing the Gamma function. The computed time correlation functions, as well as the fitted representations are shown in Figure 1. In all cases the analytical representation according to Eq. 4 provides an excellent description of the correlation functions determined from MD-simulation. All parameters necessary for describing the fitted time correlation functions are summarized in Table 1. Quite surprisingly, we find that the dominating *long-time* behavior is in all cases best represented by a mono-exponential decay, whereas the *short/medium-time* behavior (which is apparently composed of several relaxation processes) is apparently better described by a stretched exponentials with rather low Kohlrausch-exponents β around 0.3 – 0.5. The computed correlation times τ_c according to Eq. 5 are summarized in Table 2. In Figure 2 the temperature dependence of τ_c is provided as an Arrhenius-plot and

is hence given as a function of the inverse temperature. The temperature dependence of τ_c for all three systems is well described a single activation energy following

$$\tau_c(T) = \tau_{c,\infty} \cdot \exp\left(\frac{E_A}{RT}\right). \quad (6)$$

The computed activation energies, however, vary strongly between 22.2 kJ mol^{-1} for TEA-NTf₂ and 51.0 kJ mol^{-1} for TEA-MS with a hierarchy TEA-NTf₂ < TEA-TF < TEA-MS, similarly to the hierarchy of the correlation times τ_c itself observed for the temperature intervall between 300 K and 400 K (see Table 2). The observed hierarchy in correlation-times and activation energies correspondes well with the observed variation in hydrogen-bond-strength between cations and anions for those ionic liquids [1].

PIL	T/K	A_1	τ_1/ps	β_1	A_2	τ_2/ps
TEA-NTf ₂	300	0.672	50.3	0.392	0.300	277
	320	0.670	25.4	0.409	0.310	178
	340	0.649	13.0	0.424	0.339	118
	360	0.647	8.24	0.427	0.349	78.7
	380	0.656	6.06	0.433	0.342	56.0
	400	0.666	4.76	0.434	0.333	40.6
TEA-TF	300	0.520	2320	0.475	0.321	7522
	320	0.428	372	0.401	0.449	2264
	340	0.438	69.1	0.327	0.504	1025
	360	0.460	19.5	0.298	0.523	450
	380	0.476	12.4	0.307	0.511	280
	400	0.463	5.69	0.317	0.530	162
TEA-MS	300	0.361	5976	0.497	0.488	39307
	320	0.384	1759	0.504	0.456	13342
	340	0.388	323	0.406	0.493	2423
	360	0.413	41.5	0.323	0.547	891
	380	0.447	20.4	0.321	0.531	444
	400	0.479	12.0	0.328	0.515	247

Table 1: Parameters describing the time-dependent fitted reorientational correlation functions $C(t)$ according to Eq. 4 for the three different protic ionic liquids as a function of temperature.

T/K	TEA-NTf ₂ τ_c/ps	TEA-TF τ_c/ps	TEA-MS τ_c/ps
300	202	5083	23539
320	108	1540	7410
340	64.0	710	1593
360	42.2	320	603
380	29.6	192	299
400	21.8	105	164

Table 2: Integrated correlation times τ_c for the reorientational motion of the N-D bond-vector in the TEA-cation as a function of temperature T obtained for the three selected protic ionic liquids.

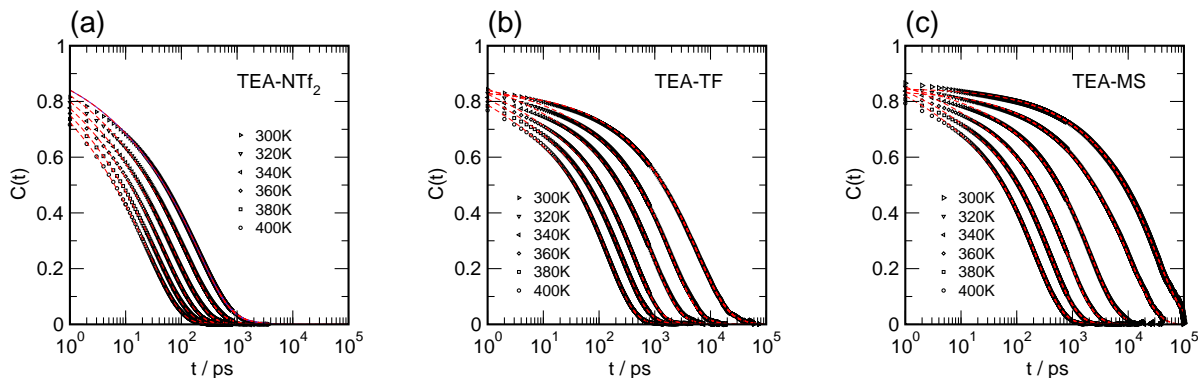


Figure 1: Temperature dependence of the time correlation functions $C(t)$ for the reorientational dynamics of the N-D vector in the TEA cation in the three studied protic ionic liquids. a) TEA-NTf₂ b) TEA-TF c) TEA-MS. Symbols indicate time correlation functions computed from MD-simulation, whereas the red dashed line represent the fitted data according to Eq. 4.

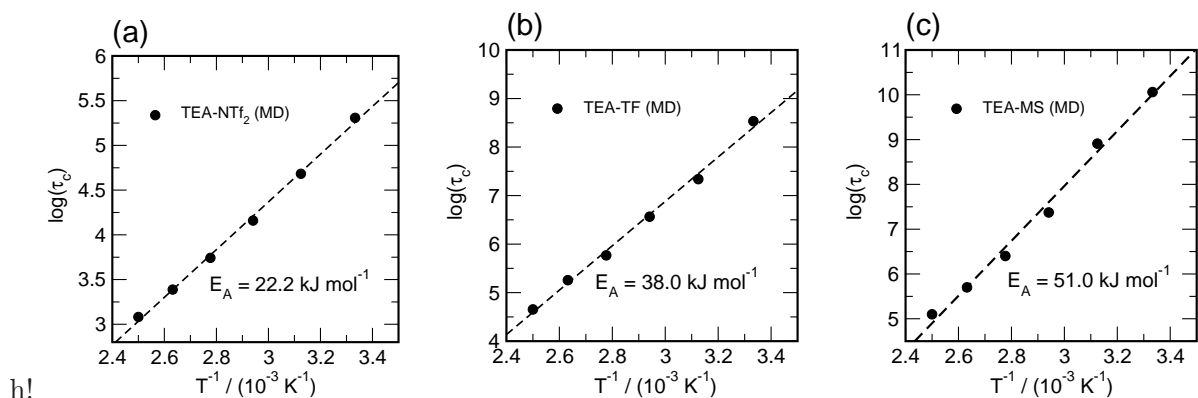


Figure 2: *Arrhenius* plots of the integrated correlation times τ_c as a function of inverse temperature for each of the investigated protic ionic liquids. a) TEA-NTf₂ b) TEA-TF c) TEA-MS.

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