

Electronic Supporting Information

Simultaneous determination of deuteron quadrupole coupling constants and rotational correlation times: The model case of hydrogen bonded ionic liquids

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SII Sample preparation

In order to prepare sample for the NMR experiments, the perdeuterated Ionic Liquid was loaded into a glass tube (5 mm o.d.; 20 mm long), connected to a high vacuum grade valve (HI-VAC). All manipulations were performed in argon atmosphere. The sample was then attached to a vacuum line and the argon was pumped off under vacuum to a final pressure above the sample of 10^{-2} Pa. To fully degas the material the sample was slowly introduced into liquid nitrogen 2-3 times, while being connected to vacuum line. After degassing, the neck of the tube was sealed off, while the material sample was maintained in liquid nitrogen in order to prevent its heating by the flame. The sealed sample was then transferred into an NMR probe for analysis with ^2H NMR spectroscopy.

SI2 Experimental

²H NMR technique

²H NMR experiments were performed at Larmor frequency $\omega_z/2\pi = 61.42$ MHz on a Bruker Avance-400 spectrometer, using a high power probe with 5 mm horizontal solenoid coil. All ²H NMR spectra were obtained by Fourier transformation of quadrature-detected phase-cycled quadrupole echo arising in the pulse sequence ($90^\circ_x - \tau_1 - 90^\circ_y - \tau_2 - \text{acquisition} - t$), where $\tau_1 = 20 \mu\text{s}$, $\tau_2 = 21 \mu\text{s}$ and t is a repetition time of the sequence during the accumulation of the NMR signal. The duration of the $\pi/2$ pulse was 1.6-1.7 μs . Spectra were typically obtained with 50 - 20000 scans with repetition time ranging from 0.5 to 15 seconds. Inversion-recovery experiments to derive spin-lattice relaxation times (T_1) were carried out using the pulse sequence ($180^\circ_x - t_v - 90^\circ_x - \tau - 90^\circ_y - \tau - \text{acquisition } n$), where t_v was a variable delay between the 180° and 90° pulses.

The temperature of the samples was controlled with a flow of nitrogen gas by a variable-temperature unit BVT-3000 with a precision of about 1 K.

It should be noted that in each the NMR experiments were conducted by first cooling the sample in the liquid nitrogen, rapidly transferring the sample in the pre-cooled probe and then heating it up to the required temperature. Such procedure allowed a perfect reproducibility of the experimental results in the solid phase.

Viscosity measurements

The dynamic viscosities (η) of pure ionic liquids were determined in the temperature range between 393 and 343 K using a microviscosimeter (Lovis 2000 ME / Anton Paar Austria) based on the rolling ball principle. The estimated accuracy of the viscosity measurements was ± 0.5 percent.

The DSC study of thermal behavior for protic ILs with trialkyl ammonium cations.

The thermal behavior for [OMs] ILs with [TEA], [THA], [TOA] cations were studied with the help of Mettler Toledo DSC 823e coupled with Huber TC125MT cooler. This cooler provides the possibility to start the DSC heating runs from 173 K. At the same time the low cooling power at the low temperature stems in behaviour artefacts on cooling (at ~ 220 K for $10 \text{ K}\cdot\text{min}^{-1}$ and at ~ 200 K for $5 \text{ K}\cdot\text{min}^{-1}$). The sample was placed in the standard non-pierced aluminium pans of $40 \mu\text{l}$ volume. The charged opened pans were put under vacuum at 330 K for 6 hours. After vacuum treatment the charged pans were sealed under dry nitrogen atmosphere (dew point < 160 K). The masses of pans and samples were determined with Sartorius MSE3.6P-000-DM microbalances with the standard uncertainty of $5 \cdot 10^{-6}$ g. The calibration of Mettler Toledo DSC 823e was checked with melting behavior of the reference samples of indium, lead, tin, gallium, bidistilled water and high purity n-octane. The temperature of fusion agreed with values better than 0.3 K and the fusion enthalpy within 1 %.

The temperature profile of investigation for all compounds was the same - cooling down to 173 K at 10, 5 or $1 \text{ K}\cdot\text{min}^{-1}$ cooling rate and annealing for 30 minutes at this temperature. After that, the sample was heated to 373 K with a rate of $10 \text{ K}\cdot\text{min}^{-1}$. When no difference in the behavior was observed, the sample was cooled with $10 \text{ K}\cdot\text{min}^{-1}$ cooling rate and annealed for 30 minutes and followed with heating at 1, 5 and $10 \text{ K}\cdot\text{min}^{-1}$. For all compounds, two samples of different masses were applied during study.

The summary of the phase transitions is given in Table S1.

Table S1. The thermodynamic parameters of observed phase transitions for studied ILs.

Ionic liquid	Phase transition	T_{trs} , K	$\Delta_{\text{trs}}H^{\circ}_{\text{m}}$, $\text{kJ}\cdot\text{mol}^{-1}$	Comments
[TEA][OMs]	cr-liquid	298.4 ± 0.5	19.8 ± 0.2	
[THA][OMs]	glass - liquid	189.8 ± 0.5	-	Small relaxation
[TOA][OMs]	glass - liquid	190.8 ± 0.3	-	peak is observed.