Static magnetic field alters properties of confined alkylammonium nitrate ionic liquids

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A B S T R A C T

Ethylammonium nitrate (EAN) and propylammonium nitrate (PAN) ionic liquids confined between polar glass plates and exposed to a strong magnetic field of 9.4 T demonstrate gradually slowing diffusivity, a process that can be reversed by removing the sample from the magnetic field. The process can be described well by the Avrami equation, which is typical for autocatalytic (particularly, nucleation controlled) processes. The transition can be stopped by freezing the sample. Cooling and heating investigations showed differences in the freezing and melting behavior of the sample depending on whether it had been exposed to the magnetic field. After exposure to the magnetic field, the sample demonstrated decrease in the ^{1}H NMR signal of residual water. ^{1}H NMR spectroscopy with presaturation demonstrates that the most probable mechanism of the decrease of the bulk water signal is adsorption of water on polar surfaces of glass plates. Generally, our findings confirm our previous suggestion that alteration of the dynamic properties of confined alkylammonium nitrate ionic liquids exposed to a magnetic field is related to the alteration of real physical-chemical phases.

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1. Introduction

Ionic liquids (ILs) are prepared from organic cations and either organic or inorganic anions [1,2]. They have been used as electrolyte materials in lithium batteries [3,4] and supercapacitors [5], as media for chemical reactions, protein separation [2,6], CO_2 absorption [7], and as lubricants [8]. Ammonium nitrates have three readily exchangeable protons on the NH_3 group of cations, therefore, they belong to a class of so called 'protic' ionic liquids [1]. EAN is the most frequently reported protic IL [1], which is used as a reaction medium, as a precipitating agent for protein separation [6], and as an electrically conductive solvent in electrochemistry [3]. Like water, EAN has a three-dimensional hydrogen-bonding network and can be used as an amphiphilic self-assembly medium [9]. Confined ILs [10–12], particularly EAN [11,13,14], have attracted special interest during the last few years. Enhanced diffusion of ethylammonium (EA) cations has been observed for EAN confined between polar glass plates [13]. It was experimentally found that both self-diffusion and NMR relaxation of EAN confined between polar glass plates reversibly alter after the sample placement in a strong (9.4 T) static magnetic field [14]. The main factors responsible for this effect are the availability of protons in the protic EAN and the

polarity of the surface, while the exchange rate of —NH_3 protons plays a crucial role in the observed processes. It has been suggested that the processes influencing the dynamics of EAN in this confinement are the phase transformations of EAN [14].

In this work, we further investigate the physical properties of confined EAN and another protic IL belonging to the same class, propylammonium nitrate (PAN), and the effect of applying a strong (9.4) static magnetic field under the same confinement conditions, i.e. between polar glass plates.

2. Materials and methods

2.1. Sample preparation

The chemical structures of ions of the studied ionic liquids are shown in Fig. 1. ILs were synthesized and characterized at Chemistry of Interfaces of Luleå University of Technology as described previously [13]. EAN and PAN are liquids at ambient conditions. The quantity of water in the synthesized ILs was <0.055 wt% as determined by Karl-Fisher titration (Metrohm 917 Karl Fischer Coulometer with HYDRANAL reagent).

NMR measurements for the bulk ionic liquids were performed by placing 300 μl of the IL in a standard 5-mm NMR glass tube. Confined ILs were prepared with glass plates arranged in a stack (see Fig. S1 in the Electronic Supporting Information, ESI). The plates (14 × 2.5 ×

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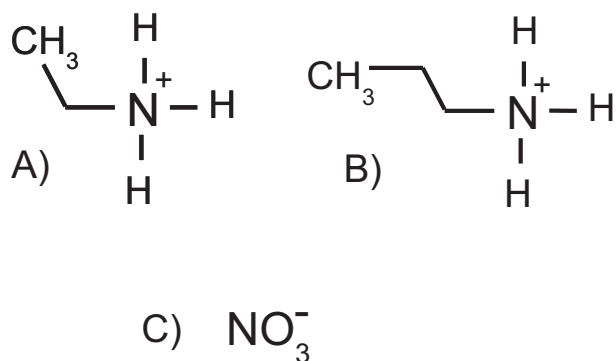   E-mail address: andrei.filippov@ltu.se (A. Filippov).

Fig. 1. Chemical structures of A) ethylammonium (EA) cation; B) propylammonium cation; and C) nitrate anion.

0.1 mm, Thermo Scientific Menzel-Gläser, Menzel GmbH, Germany) were carefully cleaned before sample preparation (see the ESI). Contact angle measurements with Milli-Q water gave a contact angle near 0°. A stack of glass plates filled with IL was prepared in a glove box in a dry N_2 atmosphere. Samples were made by adding 2 μL of an IL to the first glass plate, placing a new glass plate on top, adding 2 μL of the IL on top of this glass plate, *etc.* until the thickness of the stack reached 2.5 mm. IL that overflowed at the edges of the stack was removed by sponging. The sample consisting of a stack of *ca.* 37 glass plates was placed in a rectangular glass tube and sealed. The mean spacing between the glass plates was assessed by weighing the introduced IL, which yielded $d \sim 3.8–4.5$ μm for EAN [13]. A detailed report of the sample preparation and characterization has been described in our previous papers [13,14]. To allow equilibration of ILs inside the samples, experiments were started a week after the sample preparation.

2.2. Pulsed-field gradient NMR diffusometry

^1H NMR self-diffusion measurements were performed using a Bruker Ascend/Aeon WB 400 (Bruker BioSpin AG, Fällanden, Switzerland) NMR spectrometer with a working frequency of 400.27 MHz for ^1H, magnetic field strength of 9.4 T with magnetic field homogeneity better than $4.9 \cdot 10^{-7}$ T, using a Diff50 Pulsed-Field-Gradient (PFG) probe. An NMR solenoid ^1H insert was used to macroscopically align the plates of the sample stack at 0 and 90° with respect to the direction of the external magnetic field (the same direction as that of the PFG).

The BCU II cooling unit was used for low-temperature NMR experiments. This allows maintenance of the temperature of the NMR sample at temperatures down to approximately 230 K with precision of 1 K. The unit was calibrated using copper-constantan thermocouple.

The diffusional decays (DD) were recorded using the spin-echo (SE, at $t_d \leq 5$ ms) or the stimulated echo (StE) pulse sequences. For single-component diffusion, the form of DD can be described as follows [15,16]:for the SE and StE, respectively. Here, A is the signal intensity, τ and τ_1 are the time intervals in the pulse sequence; γ is the gyromagnetic ratio for protons; g and δ are the amplitude and the duration of the gradient pulse; $t_d = (\Delta - \delta/3)$ is the diffusion time; $\Delta = (\tau + \tau_1)$. D is the diffusion coefficient. In the measurements, the duration of the 90° pulse was $7 \cdot 10^{-6}$ s, δ was in the range of $(0.5–2) \cdot 10^{-3}$ s, τ was in the range of $(3–5) \cdot 10^{-3}$ s, and the amplitude of g was varied from 0.06 up to 29.73 T·m^{-1}. The recycle delay was 3.5 s.

As has been shown [13], restrictions (glass plates) had no effect on the D of EAN in the direction along the plates, while for diffusion normal to the plates the effect of the plates on D was perceptible at t_d longer than $3 \cdot 10^{-3}$ s. For diffusion in bulk and along the plates, D values were acquired by fitting Eqs. (1a) and (1b) to the experimental decays. For decays obtained in the direction normal to the plates at $t_d = 3$ ms, D was calculated from the equation

Most of measurements were performed at 293 K (room temperature), therefore, we did not wait until thermal equilibration of the sample in the NMR probe was reached and measurements were started directly (in 1–2 min) after placing the sample in the NMR probe, tuning and matching the probe. The time required for a single NMR diffusion measurement was around 30 s. Data were processed using Bruker Topspin 3.5 software.

2.3. ^1H NMR water presaturation experiments

Bruker's NMR pulse sequences **zgpr** (Presaturation) and **H1_3919** (Watergate 3-9-19 supersaturation) were used for ^1H presaturation experiments of —NH$_3$ protons. Duration of 90° pulses was $4 \cdot 10^{-5}$ s with a power 2.24 W. Duration of gradient pulses was $2 \cdot 10^{-3}$ s and its amplitude was 0.1062 T/m.

3. Results and discussion

In previous [13,14] and current studies we observed differences in self-diffusion and local dynamics of ammonium nitrates (mainly EAN) in their (i) bulk states, (ii) confined between polar glass plates and (iii) the system (ii) exposed in a strong static magnetic field for rather long time (*ca.* 24 h). These states were characterized as "dynamic phases" [13,14]. For the purpose of simplicity, in further discussion we use a term "phase" for ammonium nitrates in the states (i), (ii) and (iii) as I_B, I and I_{MF}, respectively, taking into account that we have not yet proven structural and thermodynamic differences between phases of EAN in these states.

3.1. Diffusivity

Placement of bulk ILs in the static magnetic field of the NMR spectrometer and systematic measurements of D during and over 24 h showed no changes in diffusivity. Therefore, it can be suggested that the bulk phases "I_B" of this class of protic ILs were maintained during magnetic field exposure according to previous findings [13,17]. The values of the diffusion coefficients (D_0) for bulk EAN and PAN are shown in Fig. 2 as dotted lines. The diffusion coefficients of cations of EAN and PAN between polar glass plates (D^*) were a factor of ~2.5 larger than those in bulk, which was observed previously by us for EAN [14]. Just after placement in the magnetic field, the diffusivity of the cations gradually decreased, as shown in Fig. 2. The process reaches saturation
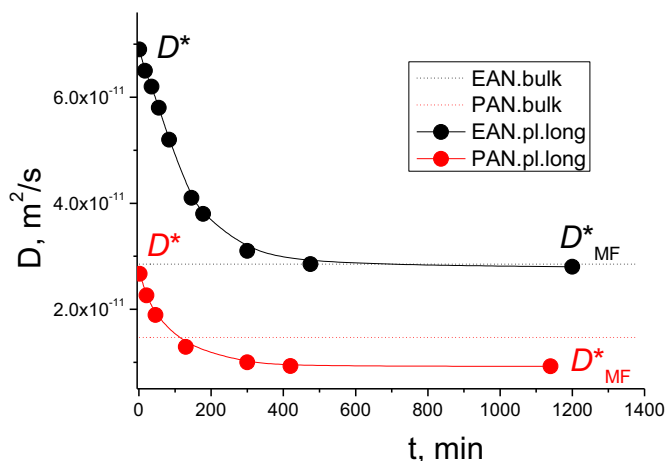

Fig. 2. A change in diffusion coefficients of cations of protic ionic liquids EAN (black) and PAN (red) after placing alkylammonium nitrate ILs confined between polar plates in a static magnetic field of 9.4 T. Diffusion coefficients were measured along the plates, diffusion time $t_d = 3$ ms. Dotted lines of different colours (black and red) correspond to D of bulk ILs (EAN and PAN, respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)