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Static magnetic field alters properties of confined alkylammonium nitrate ionic liquids

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ABSTRACT

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.

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 × 0.1 mm, Thermo Scientific Menzel-Gläser, Menzel GmbH, Germany)

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