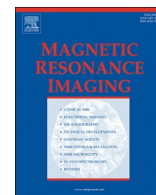




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Original Contribution

Temperature dependence of ^1H NMR chemical shifts and diffusivity of confined ethylammonium nitrate ionic liquidOleg I. Gnezdilov^a, Oleg N. Antzutkin^{b,c}, Rustam Gimatdinov^d, Andrei Filippov^{b,d,*}^a Kazan Federal University, 420008 Kazan, Russia^b Chemistry of Interfaces, Luleå University of Technology, SE-97187 Luleå, Sweden^c Department of Physics, Warwick University, Coventry CV4 7AL, UK^d Kazan State Medical University, 420012 Kazan, Russia

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ABSTRACT

Some ionic liquids (ILs) change their dynamic properties when placed in a confinement between polar surfaces (Filippov et al., Phys. Chem. Chem. Phys. 2018, 20, 6316). The diffusivities of ions and NMR relaxation times in these ILs also reversibly change under a strong static magnetic field. The mechanisms of these phenomena are not clear, but it has been suggested that they involve modified hydrogen-bonding networks formed in these ILs in the presence of polar surfaces. To obtain a better understanding of these effects, we performed temperature-dependent measurements of chemical shifts and diffusion coefficients for ethylammonium nitrate (EAN) IL in the bulk phase (I_B) and confined in layers with a thickness of $\sim 4 \mu\text{m}$ between quartz plates unexposed (I phase) and exposed (I_{MF} phase) to a static magnetic field of 9.4 T. It was shown that the NMR chemical shift of NH_3 protons of EAN in the I phase is strongly shifted upfield, $\sim 0.0145 \text{ ppm/K}$, which is due to weakening of the hydrogen-bonding network of the confined EAN. Exposure to the magnetic field leads to restitution of the hydrogen-bonding (H-bonding) network. The temperature dependences of diffusion coefficients follow the order $D(I) > D(I_B) > D(I_{MF})$ and can be described by a Vogel-Fulcher-Tammann approach with variation of the pre-exponential factor, which is determined by the strength of the H-bonding network. Confinement of EAN between plates ($I_B \rightarrow I$) is an endothermic process, while processes occurring in a magnetic field, $I \rightarrow I_{MF}$ and $I_{MF} \rightarrow I$, are exothermic and endothermic, respectively.

1. Introduction

Ionic liquids (ILs) are salts prepared from organic cations and either organic or inorganic anions that remain in a liquid state near room temperature. Their design and related properties provide novel potential applications for this new class of material [1–3]. Ethylammonium nitrate (EAN) is the most frequently reported IL [2,4], which is used as a reaction medium, as a precipitating agent for protein separation [5], and as an electrically conductive solvent in electrochemistry [6]. EAN has three readily exchangeable protons on the $-\text{NH}_3$ group of cations; therefore, they belong to a class of so-called “protic” ionic liquids, which are formed by proton transfer from an equimolar combination of a Brønsted acid and a Brønsted base [2]. Like water, EAN has a three-dimensional hydrogen-bonding (H-bonding) network, which is highly connected, dense, complex and also highly variable [7,8]. H-bonding in ILs is a secondary (after ionic bonding) structure-directing contributor [8]. Cations are the dominant H-bond donors, while anions are the

dominant H-bond acceptors. The presence of the H-bonding network affects the physicochemical properties of EAN, like many other ILs. The microstructure of protic ILs depends greatly on the hydrogen bond interactions [9]. Changes in intermolecular interactions and electronic perturbations caused by variations in hydrogen bonds can be observed from ^1H NMR chemical shifts [9,10]. Typically, higher temperatures result in weakening of the hydrogen bonds and therefore lessen the electron-withdrawing effect of the hydrogen bond acceptor on the proton [10]. As a result, the proton becomes more shielded and its chemical shift value decreases (the resonance moves “upfield”). For example, ^1H NMR chemical shifts of alkyl protons of *n*-butylammonium acetate and *n*-butylammonium nitrate are almost unchanged with increasing temperature due to the absence of hydrogen bond interactions between alkyl protons with anions, whereas those of N–H of cations decrease linearly with increasing temperature, indicating that the hydrogen bond interaction weakens gradually [9].

Confined ILs [11–17], particularly EAN [12,15,18–20], have

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