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Self-diffusion of ethylammonium nitrate ionic liquid confined between modified polar glasses

Andrei Filippov [a,b,*], Oleg I. Gnezdilov [c,d], Alexander G. Luchkin [c], Oleg N. Antzutkin [a,e]

[a] Chemistry of Interfaces, Luleå University of Technology, SE-97187 Luleå, Sweden
[b] Kazan State Medical University, 420012 Kazan, Russia
[c] Kazan Federal University, 420008 Kazan, Russia
[d] Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center, Russian Academy of Sciences, 420029 Kazan, Russia
[e] Department of Physics, Warwick University, Coventry CV4 7AL, UK

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ABSTRACT

Ethylammonium nitrate (EAN) ionic liquid confined between flat polar glass plates demonstrates variable diffusivity that is sensitive to an external static magnetic field. Outside the magnetic field, diffusivity between the plates is higher than that in the bulk. However, after placing the system in a strong static magnetic field, the diffusivity gradually decreased. These processes occur during transformations between phases formed in EAN subjected to micrometer-size restrictions outside and within the magnetic field (Filippov et al., *J. Mol. Liq.* [2018] 268, 49). In this study, we used samples of two types: (i) with roughened surface formed by treatment of the glass plates with aqueous solutions of hydrofluoric acid and (ii) with vacuum deposited TiO_2 layers with a thickness of ca. 1 μm at glass-plate edges. Neither the surface modification of the glass plates, nor the TiO_2 layers controlled thickness of EAN confined between glass-plates significantly changed the above-described effects, which have been observed in studies using untreated glass plates. Therefore, the range of systems with detected phase transformations in EAN and accompanying effects, such as accelerated diffusivity and change in diffusivity under the influence of a static magnetic field, was expanded to the systems with roughened surfaces and the systems with TiO_2 layers controlled inter-plates distances. Results of experiments with roughened surfaces additionally suggested that the phase transformation of confined EAN in the external magnetic field is isotropic in nature rather than a phase transition from "layered to bulk" structures.

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]. Alkylammonium 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 [2]. Ethylammonium nitrate (EAN) is the most frequently reported protic 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]. Like water, EAN has a three-dimensional hydrogen-bonding network and can be used as an amphiphilic self-assembly medium [7]. Confined ILs [8–12], particularly EAN [9,12–16], have attracted special interest during the last few years. Enhanced diffusion of ethylammonium (EA) cations has been observed for EAN confined between glass plates [12]. Magnetic field strength is an important external variable that may influence phase and dynamic properties of some liquid systems, such as liquid crystals with molecules having anisotropic magnetic susceptibility [17] and solid materials, such as organic-based semiconductors [18]. There are reports on magnetic ionic liquids (MILs), which contain ferromagnetic ions in their chemical structure, but no perceptible magnetic field effects have been observed for non-magnetic ionic liquids [19,20] until it was found recently that both self-diffusion and NMR relaxation of EAN and propylammonium nitrate (PAN) confined between glass plates with inter-plates distances of ca. 4 μm reversibly alter after sample placement in a strong static magnetic field [14,15]. 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 [14]. It has been suggested that the processes influencing the dynamics of EAN in this confinement are the phase transformations of EAN [14,15]. It has also been demonstrated that the process can be described well by the Avrami equation, which is typical for autocatalytic processes [15]. The transition can be stopped by freezing the sample. Cooling and heating investigations showed differences

* Corresponding author at: Chemistry of Interfaces, Luleå University of Technology, SE-97187 Luleå, Sweden.
E-mail address: andrei.filippov@ltu.se (A. Filippov).

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