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Self-diffusion in ionic liquids with nitrate anion: Effects of confinement between glass plates and static magnetic field

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ABSTRACT

Alkylammonium nitrate protic ionic liquids (ILs), when placed between flat polar borosilicate glass plates, have demonstrated enhanced diffusivity and the gradual decrease of diffusivity after exposure to an external static magnetic field (Filippov et al., 2018). This phenomenon has been explained by phase transformations taking place in the ILs. In this study, we observed similar processes occurring in systems prepared with ethylammonium nitrate confined between quartz plates. A higher content of silicon oxide in the plates does not significantly alter the phenomenon previously found in the system prepared with borosilicate glass plates. For the first time, we have observed similar effects of confinement and magnetic field on the aprotic IL, 1-ethyl-3-methylimidazolium nitrate. Substitution of the ethylammonium cation with a 1-ethyl-3-methylimidazolium cation slows down the kinetics and increases magnitude of the processes occurring in the IL exposed to a magnetic field. We suggested that the main factor determining these effects is the presence and modification of the hydrogen-bonding network in the studied protic and aprotic ILs. The process of inverse phase transformation for the confined ethylammonium nitrate after removing the sample from the magnetic field was observed and analysed.

1. Introduction

Ionic liquids (ILs) are a relatively new type of material prepared from organic cations and either organic or inorganic anions that persist in a liquid state near ambient temperature [1–3]. Protic IL is formed by the transfer of a proton from Brønsted acid to Brønsted base, while aprotic cations tend to have C—H bond as the primary H-bond donor unit [2,4]. Structures and properties of ILs at solid-IL interfaces and in confinements are of significant importance to many technological applications of the ILs, including electrochemical processes on the electrodes of batteries and electroplating, in fuel cell membranes, friction surfaces, dissolved solids, etc. [5–9]. Therefore, processes near surfaces and in confinements have attracted special interest during the last few years. It has been observed that diffusion coefficients of some nano-confined ILs in aligned carbon nanotubes [10], mesoporous carbon [11] and silicon [12,13] increases by a factor of 2–3 or even more as compared to the diffusivities of ions in the bulk ILs. This has been explained by loose packing of ions in the tight confinement [12]. Our group was the first to revealed variations in local and translational dynamic properties [14] and melting temperatures [15] of ILs confined in micrometer-size range of restrictions. Spontaneous reaction in the aprotic IL 1-ethyl-3-methylimidazolium acetate confined between glass plates, leading to the formation of a neutral chemical moiety, which was assigned as N-heterocyclic carbene has been observed [16]. Enhanced diffusion of alkylammonium cations has been observed for the protic ILs ethylammonium nitrate (EAN) and propylammoniun nitrate (PAN) confined between borosilicate glass plates [14,15]. Magnetic field strength is an important external variable that may influence the 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 ILs, which contain ferromagnetic ions in their chemical structure, but no perceptible magnetic field effects have been observed for non-magnetic ILs before [3]. Recently it was found that both self-diffusion and NMR relaxation of EAN and PAN confined between borosilicate glass plates with inter-plate distances of ca. 4 μm are reversibly altered after sample placement in a static magnetic field [15,19]. It has been demonstrated that the dynamic processes can be described well by the Avrami equation, which is typical for autocatalytic processes [15]. Recently, the same phenomena were observed in systems prepared with surface-treated borosilicate glass plates [20] and for EAN-water mixtures [21]. Underlying physical-chemical

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