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How does lithium nitrate dissolve in a protic ionic liquid?

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ABSTRACT

The structural properties of a mixture of ethylammonium nitrate (EAN), a protic ionic liquid, and lithium nitrate are explored using X-ray diffraction and reverse Monte Carlo simulation. The system is characterised by the amphiphilically driven polar–apolar domains segregation that is peculiar of EAN, whilst the lithium ions distribute in the charged domains where they undergo a further level of self-segregation, prompting for a new ion solvation mechanism in amphiphilically nanostructured ionic liquids.

1. Introduction

Ionic liquids (ILs), ionic compounds with low melting point, represent one of the most promising research fields in the last decades. Their properties, including structure, dynamics and chemical interactions, depend on the subtle interplay between coulombic and dispersive interactions. One can finely tune this balance, e.g. by changing the apolar portion, extending the alkyl chain connected to the polar heads [1–5] or replace it with a less apolar moiety (e.g. replacing alkyl with ether-like moieties [6–9], or with a fluorinated tail [10,11]) and, as it was recently observed [12,13], mixing them with inorganic salts.

Recently, some studies appeared in the literature on mixtures of ILs with inorganic salts (IS) [14–22], most of them focused on mixtures of ILs with $LiTf_2N$ (Tf_2N is the bistriflamide anion), which play an important role in electrochemical devices. These studies indicate the existence of a strong anion coordination of the lithium ion. Hence, it is very important to understand the way the lithium cation is solvated in mixtures with ILs and how it structurally organises either as a free ion or, more realistically, as a solvated species.

So far, we are not aware of structural studies of mixtures of protic ionic liquids (PILs) [23,24] (a sub-class of IL which are formed through proton transfer from an acid to a base, leading to the presence of proton–donor and proton–acceptor sites, which build up an extensive hydrogen-bonded network) and ISs. Recently some of us presented the first molecular dynamics paper on this kind of mixtures, using an OPLS all-atom force field to account for the interatomic interactions [13]. In that paper MD results were compared with experimental volumetric data, leading to an agreement better than 1.5% with experimental data. In the present contribution we describe the structure of ethylammonium nitrate (EAN, $CH_3CH_2NH_3^+\ NO_3^-$) and lithium nitrate ($LiNO_3$) mixtures, using energy dispersive X-ray diffraction (EDXD) experiments that are rationalised using the Empirical Potential Structural Refinement (EPSR) approach [25]. The mixture can be considered as a ternary system, with two cations (ethylammonium (EA) and Li) and a common anion (nitrate). At ambient conditions, EAN and $LiNO_3$ are miscible only up to ca. 0.20 $LiNO_3$ molar fraction (X) and the present study focuses on a $X_{LiNO3} = 0.155$ mixture, in order to maximise the role of lithium on affecting the EAN morphology and the extent of IS structural organisation in the PIL. EAN (Fig. 1) has been studied extensively in the last few years [26–34] and it appears that its structure is dominated by two major features: a) the amphiphilic nature of the cation that leads to the occurrence of mesoscopic tails clustering embedded into a polar mesh and b) the hydrogen bonding capability that leads to an extended network across the polar region. $LiNO_3$ addition to EAN has been recently found to affect EAN's structure only slightly [13]; on the other hand the small Li ion tends to segregate into EAN's polar domains, with the tendency to create solid-like $LiNO_3$ clusters. In order to better understand this issue and get an experimental support to this speculation, we now are extending the original study with a comparison with X-ray diffraction data. To access structural information over a spatial scale from few Å up to a few nm, we use energy dispersive X-ray diffraction (EDXD) experiments (covering a wide momentum transfer range from 0.3 up to ca. 20 $Å^{-1}$) that are modelled through

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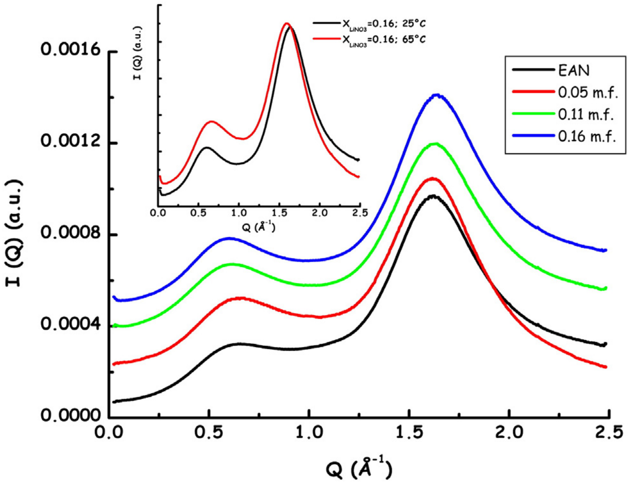

Fig. 1. SAXS data from a series of EAN–$LiNO_3$ mixtures at 25 °C (data are arbitrarily vertically shifted for sake of clarity). In the inset a comparison between the SAXS patterns from a mixture with $X_{LiNO3} = 0.16$ at 25° and 65 °C is shown.

the Empirical Potential Structural Refinement (EPSR) approach [25], and we combine this with selected results obtained by means of molecular dynamics (MD) simulations.

2. Experimental and computational details

Ethylammonium nitrate was purchased by IOLITEC with a stated purity of 97%. The material was purified from moisture under a nitrogen flux for 48 h and kept under inert atmosphere. $LiNO_3$ (>99%) was an Aldrich product and was used as received. Mixtures were prepared by weighing the two compounds inside a glove box.

Density measurements were conducted using a DSA5000 Anton Paar density and sound velocity analyzer. This apparatus is equipped with a latest-generation vibrating tube for density measurements with a resolution of 10^{-6} g/cm^3. The temperature was controlled to within 10^{-3} K by means of a Peltier module. The density metre was calibrated with dry air and distilled water at known pressure and temperature.

Small angle X-ray scattering experiments were conducted at the SWING beamline of the Soleil synchrotron, covering a Q range between 0.06 and 2.5 A^{-1}. Samples were contained in a quartz capillary and empty background was subtracted.

EDXD measurements were conducted at the Department of Chemistry at the Sapienza University of Rome facility (Italian Patent No. 01126484—23 June, 1993). For a detailed description of instrument, technique, and the experimental protocol of the data acquisition, the reader is referred to e.g. ref. [35]. The sample was contained inside a 2 mm o.d. quartz capillary and standard correction procedures were applied.

The EPSR approach has been used to model the diffraction data [25]. This is a robust approach that is based on the optimisation of the empirically derived potential that leads to a best agreement with experimental diffraction data.

We used a simulation box containing 500 EAN ion pairs and 92 $LiNO_3$ ones (EAN:$LiNO_3$ = 1:2.35; $X_{LiNO3} = 0.155$) with a density of 1.26 g/cc (box size = 43 × 43 × 43 Å). The interatomic potential used for EAN is the one that was successfully used by Atkin in a series of EPSR-based studies of PILs and their mixtures with water [27,36]. The lithium ion was modelled using a +1 charge and Lennard–Jones parameters as obtained from the EPSR routine: $\sigma = 1.505$ Å and $\varepsilon = 0.69$ kJ/mol. The interaction potential was smoothed and truncated at a distance R = 18 Å. After an equilibration of ca. 5000 steps, the EPSR optimisation was activated and further 5000 steps delivered a good agreement of the calculated diffraction pattern with the experimental one. At this stage further 15,000 steps were collected to achieve statistical accuracy on the structural observables (pair distribution functions, angular distributions etc.).

Molecular dynamics (MD) simulations of pure EAN and its solutions with $LiNO_3$ at T = 298.15 K and P = 1 atm were carried out using the GROMACS 4.5.4 package. (*D. V. D. Spoel et al., Gromacs User Manual version 4.0,* http://www.Gromacs.org*, 2005.*) With regard to the parameterisation of the ions, OPLS-AA force field, which is an all-atom version of the OPLS force field that models every hydrogen atom bonded to carbon explicitly, was used. The ethylammonium cation was modelled by using the Lennard–Jones (LJ) parameters previously reported by Umebayashi et al. [37], whilst its partial charges were evaluated by Choe et al. [38] by 6-31G** method. Lithium cation was modelled by a single site of charge +1. On the other hand, nitrate anion was parameterised as a set of seven sites, three of them being heavy sites with no charge but each of them with a third of the mass of an NO_3 anion in order to preserve the moment of inertia and centre of mass. Virtual interaction-sites are massless sites with partial charges of $q_N = +0.794$ for the nitrogen atom and $q_O = -0.598$ for the oxygen atoms [39], whose LJ parameters are, respectively, $\sigma_N = 3.496 \times 10^{-1}$ nm, $\varepsilon_N = 7.1128 \times 10^{-1}$ kJ/mol, $\sigma_O = 3.175 \times 10^{-1}$ nm and $\varepsilon_O = 8.7864 \times 10^{-1}$ kJ/mol, and were fitted in order to reproduce the experimental density. Other details of the simulation have been reported elsewhere [15].

3. Results and discussion

Preliminary studies showed that EAN–$LiNO_3$ mixtures are homogeneous up to a $X_{LiNO3} \approx 0.20$, in the EAN-rich range [13]. In this concentration range we measured the small angle X-ray diffraction patterns aiming to explore the mesoscopic order in these mixtures. Fig. 1 reports such data: it appears that all the diffraction patterns are characterised by two amorphous halos, in agreement with the results found for pure EAN by other groups [29,30,37,40]. Great interest has been captured in the last few years by the low Q peak centred at ca. 0. 66 A^{-1}, as it fingerprints the existence of a mesoscale segregation of the side tails into a sponge like morphology [26,27,29,41], similarly to what happens in conventional ionic liquids [2–6,42–50].

This peak is found also in the mixtures containing lithium salt and its position shifts towards smaller Q values, upon increasing Li-content. This finding is consistent with the insertion of lithium ions inside the polar domains formed by the charged moieties of EAN, thus increasing the size of these domains and, accordingly, the separation between these clusters. We also explored (inset of Fig. 1) the role of temperature on such a peak for the case of the Li-richest mixture ($X_{LiNO3} \approx 0.15$) and found that at 65 °C the peak occurs at higher Q value than at 25 °C, similarly to what is found for other ILs [7]. Accordingly one can deduce that increasing temperature and Li-content play two opposing roles on the characteristic size of the clusters in EAN–$LiNO_3$ mixtures. This effect will be further explored in the near future, as the other investigations in this paper are limited to the case of ambient conditions.

A $LiNO_3$-rich mixture (EAN:$LiNO_3$ = 1:2.35; $X_{LiNO3} = 0.155$) has been investigated using the EDXD technique and in Fig. 2 we report the experimental diffraction pattern at ambient conditions over a Q range between 0.3 and 20 A^{-1}. As noticed above, discussing the SAXS data, the diffraction pattern from the mixture shows a low Q feature, at ca. 0.65 Å^{-1}, fingerprinting the ethyl chain clustering [2,4,26,42,48,51]. $LiNO_3$ addition to pure EAN leads to a shift of the peak towards smaller values, suggesting that the Li ions insert into the charged network, leading to the growth of the characteristic size of the nanoheterogeneities in the mixtures. The experimental data have been described using the Empirical Potential Structural Refinement (EPSR) approach [25]. This approach allows optimising the interatomic potential upon fitting of the diffraction data. Accordingly, the output of this procedure is a sequence of simulation snapshots that leads to a diffraction pattern resembling the experimental one.

The chemical scheme indicating the atom nomenclature across the article is reported in Fig. 2. Fig. 2 reports a comparison between the

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