Association in ethylammonium nitrate-dimethyl sulfoxide mixtures: first structural and dynamical evidences.

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Abstract

Here we report the first structural and dynamic investigation on ethylammonium nitrate, a representative protic Ionic liquid, and dimethylsulfoxide. By using joined x-ray and neutron diffraction, we exploit the EPSR approach to extract structural information at atomistic level. EAN/DMSO turn out to be homogeneous at microscopic scales and indications for the existence of a structural leit motiv with stoichiometric composition 2DMSO:1EAN are found. Dielectric spectroscopy is used to access the relaxation map of the DMSO:EAN=60:40 mixture. No crystallization is detected and three relaxation processes could be characterised. Overall this study provides new indications of strict analogies between water and ethylammonium nitrate.

Introduction.

Room temperature ionic liquids (ILs) are attracting a great attention in the last decades thanks to several peculiar features.^{1–6} ILs are ionic compounds with low melting point and several have melting point below ambient condition. They are characterised by a negligible vapour pressure, high thermal and electrochemical stability and have interesting solvation properties towards different classes of materials. These are among the many reasons attracting attention on ILs; however nowadays the interest is shifting towards binary mixtures of ILs either with other ionic compounds or with molecular liquids, aiming to extend the range of appealing properties of this class of materials.^{7–14}

In this contribution we focus the attention on a specific IL, namely ethylammonium nitrate¹⁵, EAN, that is characterised by its protic nature (the ionic species are formed as a consequence of an acid-base equilibrium^{16–18}) and its mixtures with dimethylsulfoxide (DMSO).

Protic Ionic liquids (PILs) are a peculiar class of ILs. Together with the coulombic interactions and the dualism between polar and apolar moieties that are commonly found in ILs, PILs are characterised by a key role of hydrogen bonding (HB) in determining structural and dynamic properties at mesoscopic and even macroscopic level^{19–22}. In fact several analogies have been detected in the structural and dynamic properties of EAN and water, including the existence in EAN of an extended HB network that characterises the three dimensional order in this PIL.^{19,22–24} Driven by this analogy and by the peculiar behaviour of water-DMSO mixtures^{25–27} and aiming to clarify the nature of the analogies between water and EAN, we are presently undertaking a detailed characterization of structural and dynamic properties of EAN-DMSO mixtures, using x-ray/neutron scattering experiments, dielectric and Raman/IR spectroscopies and Quasi elastic neutron scattering. In this first contribution, we present results stemming from x-ray/neutron diffraction as well as dielectric spectroscopy studies, addressing interesting features in the structural and dynamic properties of a specific EAN-DMSO mixture.

EAN mixtures with other compounds that might be related to the present study have been studied only by a few groups. Atkin explored the structural properties of EAN-water mixtures⁸ as well as rheological properties of EAN-EAFormate mixtures²⁸; Drummond investigated structural properties of a series of PILs, including EAN, mixed with alcohols²⁹; Mancini investigated different mixtures of EAN with DMSO, MeOH and Acetonitrile³⁰; Lemordant explored the rheological properties of EAN-MeOH mixtures³¹; some of us recently studied binary mixtures of EAN with

LiNO_3 ³² and recently reported on the peculiar mesoscopic structural organization in EAN-methanol mixtures¹⁴.

Many of the observed properties in these mixtures strongly depend on the high level of mesoscopic order occurring in ILs^{9,33–38} in general and in EAN in particular^{23,39,40}. It is nowadays very well established that ILs are characterised by an enhanced level of structural correlation over supramolecular distances. Apart from preliminary indications in this direction, the first experimental direct observation for this order was detected in the family of alkyl imidazolium salts in 2007, using x-ray scattering.³³ These experiments highlighted the existence of a low momentum transfer (Q) peak that fingerprints the existence of structural correlations of the order of a few tens of Angstroms.⁴¹ Since then this diffraction feature has been ubiquitously found in ILs and has been related to the inherent amphiphilic nature of IL that leads to a polar vs apolar segregation in the bulk state.^{23,41–45} When the polar vs apolar contrast is limited (e.g. by increasing the polarity of the apolar moieties) the segregation does not occur and the diffraction feature disappears. Recently a series of studies addressed the role of additives (ionic or molecular) in affecting the mesoscopic order in ILs.^{10,14,46–48}

So far no study exists on the role played by DMSO in affecting the structure of ILs and in the present study we will explore a specific concentration in the EAN-DMSO system, namely 40% molar fraction in EAN content. A more extended study on other concentrations will be present later on.

DMSO is among the most used molecular liquids. It plays a very specific role in several applications, including bio-related ones. Among the most interesting properties of DMSO, we remind the major role played by this compound on the melting point of mixtures with water.^{25,26,49} Binary mixtures DMSO-water are characterised by a complex phase diagram with the formation of an eutectic. At 33% DMSO, the melting point drops to -75°C ²⁵, thus making these binary mixtures extremely interesting for both applicative and basic science issues. Due to the strong water-DMSO interactions (that are the consequence of the large dipole of the sulfoxide group), DMSO additions are able to largely affect the structure and dynamics of the mixtures.^{26,49–57} Much of these effects are related to the interaction of the sulfoxide dipole with the hydrogen bonding network in water. Accordingly, given the role of HB in affecting the short-to-medium range order in EAN^{19,22,23,58–60}, we speculate that DMSO might also interact with the HB network in EAN and affect EAN's properties similarly to what happens with water.

As a matter of fact a preliminary screening allowed verifying that EAN-DMSO mixtures in the range $0.3 \leq X_{\text{EAN}} \leq 0.8$ can be easily supercooled down to -100°C without intervening crystallization (neat EAN crystallises at 12°C , while DMSO crystallises at 18°C), thus confirming the original hypothesis that DMSO might play a major role on EAN's melting point, presumably as a consequence of its interaction with EAN's HB network, similarly to the water-DMSO behaviour. Driven by these evidences we undertook a preliminary structural and dynamic investigation on a binary mixture with $X_{\text{EAN}}=0.4$, using joint x-ray and neutron diffraction and dielectric spectroscopy. In the following we report the findings from this study.

Experimental and computational details.

Ethylammonium nitrate (EAN) was purchased from Iolitec with a nominal content of $>97\%$. The sample was treated at 40°C for two days under high vacuum to remove moisture. The water content, determined by NMR analysis in dimethylsulphoxide (DMSO)- d_6 , was below 0.6% wt. Ammonium deuterated EAN (d_3 -EAN) was prepared by repeated exchange with excess D_2O , followed by water removal by using a rotary evaporator first and after keeping the salt under high vacuum at 40°C for two days. 1H -NMR experiments indicate that, on average, 2.4 out of 3 amino hydrogens are replaced with deuterium.

DMSO and fully deuterated (d_6 -) DMSO were purchased from Sigma-Aldrich with nominal concentrations: 99.9 (anhydrous) and 99.96% respectively. They were used as received.

Mixtures were prepared by weight under inert atmosphere inside a glove box and solutions were kept under N_2 to prevent moisture absorption.

Density measurements were conducted using a DM45 Mettler-Toledo density-meter. This apparatus is equipped with a vibrating tube with a resolution of 10^{-5} g/cc. The temperature was controlled to within 10^{-3} K by means of a Peltier module. The density meter was calibrated with dry air and degassed-distilled water at ambient pressure and temperature.

Energy dispersed x-ray diffraction (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. ⁶¹. The sample was contained inside a 2 mm o.d. quartz capillary and standard correction procedures were applied.

Neutron scattering experiments were conducted at the SANDALS instrument at ISIS. The sample was contained in 1 mm thick TiZr cells. Standard corrections and background subtractions were applied. The neutron wavelength range is 0.05–4.95 Å, and data were collected over the Q range between 0.1 and 50 Å⁻¹. An EAN-DMSO mixture with nominal X_{EAN}=0.4 was measured at 25°C using the following isotopic substitution: CH₃CH₂ND₃NO₃/(CD₃)₂SO.

Small-Wide Angle x-ray scattering data were collected at the 11-ID-C beamline at the Advanced Photon Source (APS) of the Argonne National Laboratory (ANL) facility. Samples were contained in a 2 mm o.d. quartz capillary and held on a static sample holder. Standard treatments were applied to the collected data, including background subtraction.

The Empirical Potential for Structural Refinement (EPSR) approach has been used to model the diffraction data.⁶² This is a robust approach that is based on the optimization of the empirically derived potential that leads to a best agreement with experimental diffraction data. We used a simulation box containing 100 EAN ion pairs and 150 DMSO molecules (EAN:DMSO=1:1.5; X_{EAN}=0.4) with a density of 1.16015 g/cc (box size=L=32x32x32 Å, with 2π/L=0.2 Å⁻¹, being the smallest achievable momentum transfer value in the simulation).

The potential used for the EAN compound is the one that was successfully used by Atkin in a series of EPSR-based studies of PILs²³ and their mixtures with water⁸. The DMSO molecular liquid was modelled using the geometry and potential parameters arising from the detailed characterizations developed by Cordeiro and Soper.^{56,63–68} After an equilibration of ca. 10,000 steps, the EPSR optimization was activated and further 5000 steps delivered a good agreement of the calculated diffraction pattern with the experimental one. At this stage further 15000 steps were collected to achieve statistical accuracy.

Several observables were extracted from these snapshots, including pair distribution functions (pdf), angular distribution functions (adf), and spatial distribution functions (sdf) using either the EPSR built in routines or the software TRAVIS^{69,70}.

Dielectric spectroscopy data were collected between 140 and 250 K in the range 0.01 to 10⁷ Hz, applying the gain-phase analysis technique with a Solartron SI-1260 analyzer and a Novo-Control BDS 4000 spectrometer. The sample was sandwiched between two gold plated flat electrodes, with diameter of 20 mm and with a sample thickness of 50 μm. The temperature was controlled by a Quatro cryosystem.

Preliminary DSC measurements indicate the glass transition of EAN-DMSO mixtures with X_{EAN}=0.4 at 170±2 K.

Results and Discussion.

Small-Wide Angle x-ray (SWAXS) data collected at beamline 11-ID-C at 298 K over the whole

Figure 1. Small-Wide Angle x-ray scattering (S-WAXS) data from binary mixtures of ethylammonium nitrate (EAN) and dimethylsulfoxide (DMSO) at ambient conditions, as a function of the concentration.

concentration range are reported in Figure 1 and they show the concentration dependence of the low Q portion of the diffraction patterns. It can be observed that similarly to neat EAN, EAN-rich mixtures are characterised by a low Q peak centred at ca. $0.65 \text{ \AA}^{-1}$, that fingerprints the locally pseudo-lamellar organization of the PIL.^{23,39,60,71,72} This diffraction feature progressively shifts

Scheme 1. Chemical representation and nomenclature of the atomic species involved in the study: (from left to right) nitrate, ethylammonium (EA) and dimethylsulfoxide (DMSO).

towards higher Q values and decreases its amplitude upon DMSO addition.

Moreover it is noteworthy that at lower Q values than $0.4 \text{ \AA}^{-1}$ no excess SWAXS amplitude is observed over the whole concentration range, thus providing the indication that no indication of mesoscopic phase separation is found, that is EAN-DMSO mixtures are homogenous over a spatial scale of a few nm. However, we notice that neutron scattering data (vide infra) will indicate the existence for an amorphous halo at ca. $0.8 \text{ \AA}^{-1}$, where x-ray scattering are almost featureless, thus

indicating that contrast might play a major role in the determination of the existence of this diffraction feature.

The experimental x-ray and neutron diffraction data collected at the in house EDXD facility and the SANDALS beamline at ISIS at 298 K, respectively, are presented in Figure 2, together with their simultaneous EPSR-based modelling. Symbols refer to experimental data, while the continuous line refers to the modelling. The EPSR description of the data is very good over all the momentum

transfer range, thus validating the original potential choice and the following empirical refinement.

The Empirical Potential for Structural Refinement (ESPR) approach allows extracting several structural observables, including pair and angular distribution functions (pdf and adf, respectively) from a series of simulation snapshots that are compatible with the scattering data collected on the samples. In the following we will discuss these observables.

In Figures 3 a)-b) a comparison between selected pdfs from pure EAN, pure DMSO and the present EAN-DMSO mixture are reported (see scheme 1 for the atomic nomenclature). The EAN's pdfs

Figure 3 a). Comparison between EPSR-derived pair distribution functions for selected DMSO-DMSO correlations in the case of neat DMSO (black line) and EAN-DMSO ($X_{\text{EAN}}=0.4$) mixture (red line).

have been obtained from a previous work that essentially reproduces the results presented by Atkin and coworkers a few years ago²³, while the DMSO pdfs have been obtained using the P2 potential used by Soper.⁶⁸ Figure 3 a) refers to DMSO-DMSO correlations, either in neat DMSO or in the mixture: it can be appreciated that all the structural correlations are affected by the presence of EAN. Reports from Skaf^{73,74} and McLain⁵⁶ show that DMSO when mixed with methanol tends to retain its structure, while large changes in DMSO-DMSO pdfs occur when mixing with water. In this respect the similitude between water and EAN occurs again in their capability of affecting DMSO self correlations. At the probed concentration, we observe that especially Od-Od and Cd-Cd are largely affected by the presence of EAN. For example in the case of Od-Od correlations, it appears that upon adding EAN to pure DMSO, a distinct shoulder develops at ca. 3.5-4 Å. This feature reminds of a similar occurrence in DMSO-water mixtures, where the shoulder is associated to enhanced DMSO-DMSO correlations due to an hydrophilic association mediated by hydrogen bonding with a third water molecule. We will later show that this is the case also for EAN-DMSO mixtures.

Figure 3 b). Comparison between EPSR-derived pair distribution functions for selected EAN-EAN correlations in the case of neat EAN (black line) and EAN-DMSO ($X_{\text{EAN}}=0.4$) mixture (red line). Also shown curves for C2-Cd (blue line) and Cd-Cd (green line).

Another large effect of EAN addition is the decrease of DMSO's Cd-Cd correlations at ca. 4 Å. This evidence supports the view that no hydrophobic aggregation predominates in this mixture, as previously proposed on the basis of the Od-Od pdfs data.

EAN-EAN correlations are also affected by the addition of an excess of DMSO. In Figure 3 b) selected pdfs are reported. What seems to be largely influenced by DMSO are ammonium-nitrate and C2-C2 (the terminal EA's methyl groups) correlations. In particular cation-anion correlations seem to be enhanced by DMSO addition, while the terminal methyl groups are losing the correlation that they experienced in neat EAN. In the figure, we report also two additional carbon-carbon pdfs, namely C2-Cd and Cd-Cd. It clearly emerges that while EA-EA methyl groups correlations decrease when adding DMSO, and similarly (as above mentioned) DMSO-DMSO Cd-Cd correlations are not as strong as in neat DMSO, on the other hand the C2-Cd pdf has a quite strong peak centred at 3.8 Å, thus indicating a substantial structural correlation between the methyl groups from DMSO and EA. This observation although compatible with a apolar moieties segregation model, is most probably to be interpreted as a topological consequence of the strong, hydrogen binding mediated, correlation between EA and DMSO. Accordingly this would be the consequence of an hydrophilic interaction rather than fingerprinting an hydrophobic association.

In Figure 4 a), we show a combined pdf/adf related to the existence of hydrogen bonding between the ammonium hydrogen atoms and the nitrate's oxygen in the EAN-DMSO mixture.

Figure 4 a). Combined angular (N1-H1 $\cdots$ OO) and radial (H1 $\cdots$ OO) distribution functions in the EAN-DMSO mixture, plotting the joint probability. In the upper inset the $g(r)$ N1-H1 $\cdots$ OO is plotted; in the right inset, the angular distribution function for the angle N1-H1 $\cdots$ OO is plotted under the condition $2.3 < r_{\text{H1}\cdots\text{OO}} (\text{\AA}) < 2.7$.

Analogously in figure 4 b), the corresponding functions are plotted for the correlations between the

Figure 4 b) Combined angular (N1-H1 $\cdots$ OD) and radial (H1 $\cdots$ OD) distribution functions in the EAN-DMSO mixture, plotting the joint probability. In the upper inset the $g(r)$ N1-H1 $\cdots$ OD is plotted; in the right inset, the angular distribution function for the angle N1-H1 $\cdots$ OD is plotted under the condition $2.1 < r_{\text{H1}\cdots\text{OD}} (\text{\AA}) < 2.7$.

ammonium hydrogen atoms and the DMSO's oxygen.

It can be appreciated the existence of a good extent of HB between these hydrogens with both the nitrate and DMSO acceptor sites. These HBs are, however quite long ($r_{\text{Od-H1}}=2.38 \text{ \AA}$ and $r_{\text{OO-H1}}=2.53 \text{ \AA}$) and not linear (angular distribution peak centred at ca. 135°). These correspond to moderate interactions⁷⁵ between both the nitrate and the DMSO with the ammonium ion. On average 1.4 DMSO molecules coordinate the ammonium ion and ca. five nitrate oxygens surround

Figure 5. Distribution of H-bonds for the EAN-DMSO mixture ($X_{\text{EAN}}=0.4$). The fraction of either DMSO's (black histogram) or nitrate's (red histogram) oxygen atoms around a central ammonium cation is reported.

the counterion. For comparison, in neat EAN, on average six oxygen atoms (belonging to the nitrate) coordinate the ammonium cation. Accordingly in the present mixtures the average number of coordinating oxygen atoms around the ammonium head resembles the one of neat EAN. In Figure 5, we show the distribution of coordination numbers around a central ammonium ion from either the DMSO's or the nitrate's oxygen atoms. One can observe that the majority of DMSO coordinate with an ammonium cation with one HB (ca. 40%), but also two (30%) or even three (10%) DMSO molecules can be found coordinating the ammonium with an HB. This behaviour is very similar to the one reported for water-DMSO mixtures⁷³ but strongly different from the one of methanol-DMSO mixtures⁷⁴. In particular while DMSO-CH₃OH tend to associate with a 1:1 stoichiometry that is driven by one hydrogen bond between the two species, on the other hand, water and DMSO have a more complex interspecies association mechanism that depends on the mixture concentration. In DMSO-rich mixtures the 2DMSO:1H₂O associated trimer is formed: this is supported by two HB between DMSO and water, the latter molecule bridging the DMSO ones. This leads to an enhanced correlation between the DMSO molecules that is fingerprinted by a distinct shoulder in the Od-Od $g(r)$ at $4.3 \text{ \AA}$. We notice that the same enhanced structural correlation is found in the present EAN-DMSO mixture: in comparison with neat DMSO, in the mixture the Od-Od $g(r)$ shows a distinct shoulder centred at ca. $3.8 \text{ \AA}$ (see Figure 3 a). Accordingly a recurrent structural leit-motif occurring in this mixture is the one where one central ammonium cation is

coordinated through two HBs by two DSMO molecules that are brought together to a Od-Od distance of the order of 3.8 Å, as consequence of hydrophilic association, rather than hydrophobic clustering. This observation is a further confirmation of the analogies between water and EAN: when interacting with DMSO these two compounds are leading to comparable associated entities.

In Figures 6 a) and b) the imaginary part of the dielectric modulus M'' of the EAN-DMSO mixture with $X_{\text{EAN}}=0.4$ is shown as a function of frequency and temperature, respectively. Upon cooling the sample from room condition down to 128 K no evidences of crystallization were detected at the

Figure 6 a). Imaginary part of the complex electric modulus, $M''(f)$, of EAN-DMSO ($X_{\text{EAN}}=0.4$) versus frequency at ambient pressure and constant temperature with temperature in the range 208-128 K.

Figure 6 b). Imaginary part of the complex electric modulus, $M''(f)$, of EAN-DMSO ($X_{\text{EAN}}=0.4$) versus temperature at ambient pressure and constant frequencies with temperature in the range 208-128 K. The different curves refer to isochronal conditions at frequencies: $\log f=n$, with $n=-2, -1, \dots, 6$.

cooling rate typical of this experiment (approximately 6K/hour). The spectra indicate the existence of a strong peak dominating the accessible dynamic window between 208 and 170 K, corresponding to the main conductivity relaxation often termed as sigma, σ -process. This process is generally (but this is not always the case) coupled to the primary, α process. Notably two further processes can be detected with much weaker amplitude. A secondary process, hereinafter termed as β -process, can be

distinctly observed below 160 K in the frequency window $\log f < 1$, with a peak width of ca. two decades; a further process can be detected starting at 176 K as a very large peak with a width that at the lowest temperature spans almost the whole dynamic window (ca. 6 decades): hereinafter this will be indicated as the γ -process. We mention that a recent dielectric study of DMSO-water mixtures highlighted the existence of two different relaxation processes entering the present dynamic window between 195 and 147 K.⁵³

In Figure 7, we show a representative fit of the dielectric data at 173 K, using three different contributions accounting for the three processes, σ , β and γ , respectively. We modelled the three processes using the Fourier Transform of the stretched exponential, directly in the frequency domain.^{76,77} In the time domain the relaxation process is described as: $\phi(t) = \exp[-(t/\tau)^\beta]$, where τ is

Figure 7. Representative example of the fitting of the imaginary part of the complex electric modulus, $M''(f)$, of EAN-DMSO ($X_{\text{EAN}}=0.4$) versus frequency at ambient pressure and $T=173$ K. The fitting is done using three KWW curves (see the text for details).

the characteristic temporal extent of the relaxation, while β is a parameter accounting for deviations from a purely exponential relaxation. Typical values for β range between 0.2 and 1, while a value of one indicates a purely exponential relaxation, smaller values are related to more and more collective relaxation processes.^{78,79} Depending on the β value, the average relaxation time for the relaxation is given by: $\langle \tau \rangle = \tau/\beta \Gamma(1/\beta)$, where $\Gamma(x)$ is the gamma function. Accordingly, the fitting of the data plotted in Figure 6 a) leads to the relaxation map for the studied mixture as reported in figure 8, where the temperature dependence of the average time scale for the three relaxation processes is plotted in an Arrhenius plot. It emerges that the σ process follows a non-linear trend that was modelled with a Vogel-Fulcher-Tamman (VFT) law: $\langle \tau \rangle = \tau_0 \exp[DT_0/(T-T_0)]$, where τ_0 , D and T_0 are fitting parameters.⁸⁰⁻⁸² In the specific case shown in Figure 8, one obtains: $\tau_0=10^{-15.1}$ s, $D=9.4$ and $T_0=137.7$ K. The two secondary processes, β and γ , which are modelled with an Arrhenius process ($\langle \tau \rangle = \tau_0 \exp[E_{\text{act}}/K_B T]$), are found to have comparable activations energies: 46.0 and 43.8

kJ/mol, respectively. A more complete rationalisation of these findings will be present in the near

Figure 8. Relaxation map obtained from the fitting of the imaginary part of the complex electric modulus, $M''(f)$, of EAN-DMSO ($X_{\text{EAN}}=0.4$) at ambient pressure, using three different KWW terms. The lines refer to either the VTF (black line) or the Arrhenius (red and blue lines) models to account for the relaxations' temperature dependence.

future, aiming at comparing these results with findings from mixtures at other concentrations.

Conclusion.

In this report we describe a series of structural and dynamic properties of ethylammonium nitrate / dimethylsulfoxide mixtures. To our knowledge this is the first contribution providing comparable information on EAN-DMSO mixtures. While a more complete and detailed investigation will be reported in the near future, here we can already provide some sound conclusions:

- EAN-DMSO mixtures are homogeneous over the whole concentration window at ambient conditions: no evidences of phase separation, even in the mesoscopic spatial scale are observed.
- These mixtures are characterised by an interesting phase diagram: a large concentration window exists where, similarly to water-DMSO mixtures, EAN-DMSO do not crystallise upon cooling; here we reported on the relaxation processes that can be dielectrically detected in the amorphous phase from room temperature down to 120 K, without intervening crystallization.
- From a structural point of view, these homogeneous mixtures are characterized by a thorough intermixing between the two components that interact mostly through hydrogen bonding.
- The multiple HB donor/acceptor capabilities of the EA and DMSO, respectively leads to the solvation of EA by one, two or even three DMSO molecules in a competition with the nitrate anions. These complex interactions lead to the establishment of a well defined

structural leit motiv with a EAN:DMSO=1:2 stoichiometry that resembles the one detected in similarly DMSO rich water DMSO mixtures.

- These preliminary results provide new original indication on further levels of analogies between EAN and water. Furthermore the peculiar phase behaviour of EAN-DMSO that will be better characterised in the near future opens the way to new interesting applications of this binary system in a variety of fields, including bio-pharmaceutical, extraction and cryogenics.

Acknowledgements.

This work was done within the Agreement No. 01/9001 between CCLRC and CNR, concerning collaboration in scientific research at the spallation neutron source ISIS and with partial financial support of CNR. Use of the Advanced Photon Source, beam line 11IDC, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. A.T. thanks Dr. Y. Ren and R. Spence for their support during experiments at APS and Dr. S. Imberti for her support during the experiment at ISIS as well as for the competent training on the use of analysis tools. A.T. acknowledges support from FIRB (RBFR086BOQ) and PRIN (2009WHPHRH). We would like to acknowledge the kind support in the framework of the COST Action EXIL - Exchange on Ionic Liquids (CM1206) which allowed a fruitful exchange for M. Macchiagodena.

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