ARTICLES

Nanoscale Segregation in Room Temperature Ionic Liquids[†]

Alessandro Triolo,*,‡ Olga Russina,§ Hans-Jurgen Bleif,§ and Emanuela Di Cola∥

*Istituto per i Processi Chimico-Fisici, Consiglio Nazionale delle Ricerche, via La Farina, 237, I-98123
Messina, Italy, Hahn-Meitner Institut, Glienicker str. 100, D-14109 Berlin, Germany, and
ESRF, 6 rue Jules Horowitz, BP 220, F-38043 Grenoble Cedex, France*

Room-temperature ionic liquids (RTILs) are organic salts that are characterized by low melting points. They are considered to possess a homogeneous microscopic structure. We provide the first experimental evidence of the existence of nanoscale heterogeneities in neat liquid and supercooled RTILs, such as 1-alkyl-3-methyl imidazolium-based salts, using X-ray diffraction. These heterogeneities are of the order of a few nanometers and their size is proportional to the alkyl chain length. These results provide strong support to the findings from recent molecular dynamics simulations, which proposed the occurrence of nanostructures in RTILs, as a consequence of alkyl chains segregation. Moreover, our study addresses the issue of the temperature dependence of the heterogeneities size, showing a behavior that resembles the density one only below the glass transition, thus suggesting a complex behavior above this temperature. These results will provide a novel interpretation approach for the unique chemical physical properties of RTILs.

Introduction

Room-temperature ionic liquids (RTILs)[1−4] are salts with low melting point, typically below 100 °C. Their chemical structure includes a bulky cation, such as 1-alkyl-3-methyl imidazolium (hereinafter indicated as C*n*mim), and a fluorinated anion, such as BF_4^- or PF_6^-. Such a chemical architecture leads to a very low melting point (but examples exist, where no crystallization is observed, e.g., in [C4mim][BF_4]) and a wide temperature window where the liquid state is stable. These features together with the negligible vapor pressure make these liquids ideal solvents for a wide range of applications, including synthesis, biocatalysis, electrochemistry, etc.[5−12] Moreover, the chemical physical properties of RTILs can be easily modulated, changing the alkyl chain length and the nature of the anion, thus leading to the definition of *designer solvents* for these liquids.[4,13−15]

Considering a given anion, X, the phase diagrams of the salts obtained increasing the alkyl chain length, *n*, in [C*n*mim][X] show a great degree of complexity.[16−18] For example, in the case of X = [BF_4^-], a detailed investigation[16] has shown the existence of three alkyl chain length regimes: (a) short chains ($n < 3$) lead to salts with strong interactions, which are characterized by a distinct crystalline behavior with relatively high melting points; (b) intermediate alkyl chain lengths ($3 < n < 10$) lead to a wide liquid range, with low freezing points, and the tendency to form glasses upon cooling; (c) long alkyl chain lengths ($n > 10$) salts are characterized by a complex crystalline behavior, typically showing mesomorphism; their morphology is influenced by hydrophilic and hydrophobic

behavior of the charged portions and the alkyl tail, respectively, leading to microphase separation.

It is commonly assumed that intermediate chain length salts, such as 1-butyl-3-methyl imidazolium tetrafluoroborate, [C4mim]-[BF_4],[16] are structurally homogeneous in their liquid and supercooled states where they are finding a progressively increasing number of smart applications. Many studies on these neoteric solvents consider them merely as simple molten salts and only recently a number of simulation studies revealed the perspective that a substantial structural heterogeneity may characterize these liquids.[19−22]

Short-range order in liquid [C1mim]-based RTILs has been found to be mainly related to electrostatic and hydrogen bond interactions, leading to the formation of charge ordering over two or three coordination shells.[23,24] The existence of some degree of order in longer alkyl chain RTILs ([C*n*mim]X with $12 \leq n \leq 18$) in the molten state has also been observed.[16−18] However, so far, no experimental study exists addressing the existence of structural correlations in intermediate alkyl chain length (IACL) RTILs ([C*n*mim] with $4 \leq n \leq 10$), whose morphology is commonly considered as fully isotropic and homogeneous.[16]

Recently, a number of molecular dynamics (MD) simulation studies identified the occurrence of nanoscale segregation in IACL RTILs, as due to the alkyl moieties aggregation.[19−22] This behavior if experimentally confirmed would provide new interpretation approaches to the peculiar chemical-physical properties of these liquids.

In this report we provide the first experimental evidence of the existence of nanoscale segregation in IACL RTILs, using X-ray diffraction, a technique which allows probing of spatial correlations of the order of tens of Angstroms. This finding will require further investigations both at the theoretical and

experimental levels to better rationalize the behavior of RTILs in terms of their nanosegregated morphological organization.

Experimental Section

The employed RTILs are commercial products that were purchased either from Merck (chloride salts) or from IOLITEC (tetrafluoroborate salts). The tetrafluoroborate salts were kept for at least 3 months under vacuum at room temperature to reduce the moisture content.

[C4mim]Cl was molten under vacuum at ca. 60 °C and kept in these conditions for 1 day. Then the sample was kept under vacuum at room temperature: under these conditions, the corresponding liquid salt remained in this state for periods of weeks, without any indications of crystallization. The same treatment was applied to 1-allyl-3-methyl imidazolium chloride (hereinafter indicated as [C3mim]Cl), which has been purchased from IOLITEC.

[C6mim]Cl, [C8mim]Cl, and [C10mim]Cl were purchased as viscous liquids. They were kept under vacuum at 60 °C for 1 day and subsequently kept at room temperature under vacuum, without any occurrence of crystallization for extended periods of many weeks.

WAXS data were collected using a low-temperature Guinier diffractometer manufactured by Huber (type 645), operating at the wavelength $\lambda = 1.54$ Å. The sample was sandwiched between two amorphous plastic foils, whose contribution was subsequently subtracted. The instrumental setup allowed collecting data from 100 K up to room temperature, covering a Q range between 0.25 and 5.0 Å^{-1}.

X-ray diffraction data were also collected at the ID02 beamline at the European Synchrotron Radiation Facility (ESRF), using an instrumental setup which allows covering the momentum range between 0.01 and 0.9 Å^{-1}. Measurements were collected at room temperature, using a thermostated bath, and the samples were kept in a temperature-controlled flow-through cell, with internal diameter of 1.9 mm. With this sample environment, sample and solvent scattering are measured inside the same capillary, thus allowing reliable empty cell subtraction. Data were converted to absolute intensity values, by means of normalization with the scattering from water contained in a 2.0 mm capillary at 25 °C, using an incoming beam with energy 12.5 keV.

Results and Discussion

The X-ray diffraction patterns from the series of chloride salts at room temperature are plotted in Figure 1. We limit our description to the lower Q range, aiming to describe shorter range correlations in a subsequent report. In the reported Q range, the most striking feature is the occurrence of diffraction peaks in some of the intermediate alkyl chain length salts. In particular, it can be observed that while [C3mim]Cl shows a monotonously increasing signal, all the other salts (i.e., [C4mim]-Cl, [C6mim]Cl, [C8mim]Cl, and [C10mim]Cl) show a peak whose position strongly depends on the alkyl chain length.

This is the first experimental indication of the existence of a nanoscale ordering in RTILs with intermediate alkyl chain length.

In the inset of Figure 1, the alkyl chain length dependence of the spatial correlation, L, corresponding to the interference peak position, Q_{MAX}, is reported ($L = 2\pi/Q_{MAX}$). The observed spatial correlations range from 13 to 27 Å for the investigated RTILs, indicating the existence of ordering at the nanometer scale. This ordering strongly depends on the alkyl chain length: the reported straight line corresponds to a linear fit
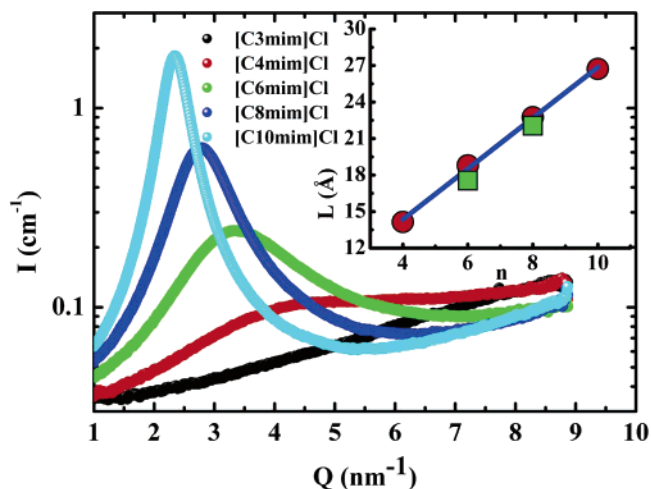

Figure 1. X-ray diffraction patterns from the series of supercooled liquid RTILs: [C$n$mim]Cl, $n = 3, 4, 6, 8, 10$, at 25 °C. In the inset the spatial correlation $L = 2\pi/Q_{MAX}$, Q_{MAX} being the interference peak position, is plotted (circles) as a function of n, the alkyl chain length, for $n \geq 4$. The corresponding data are also reported for the cases $n = 6$ and 8 for [C$n$mim][BF$_4$] (squares).
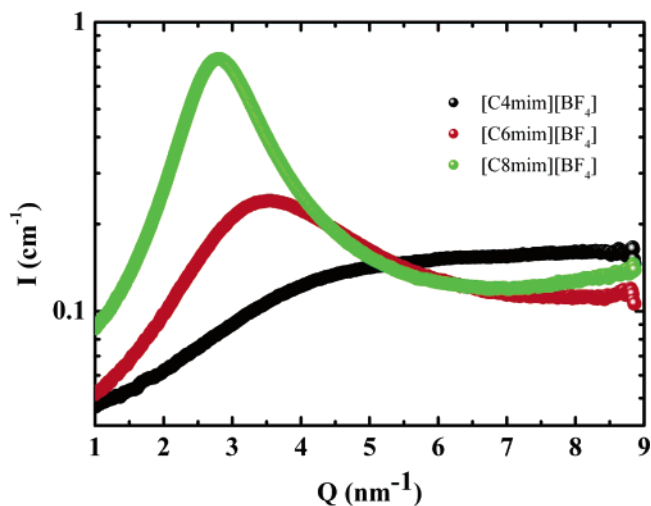

Figure 2. X-ray diffraction patterns from the series of liquid RTILs [C$n$mim][BF$_4$], $n = 4, 6, 8$, at 25 °C.

which nicely describes the growth of the spatial correlation upon increasing the alkyl chain length, with an increase of 2.1 Å per $-CH_2-$ unit.

The finding that supercooled chloride-based RTILs show a high degree of nanoscale organization is outstanding, as liquid and supercooled RTILs with intermediate alkyl chain length are generally considered to be morphologically homogeneous.

To confirm these findings on a different set of RTILs, we also measured the X-ray diffraction pattern from [BF$_4$]-based RTILs, namely, [C4mim][BF$_4$], [C6mim][BF$_4$], and [C8mim]-[BF$_4$]. These salts are thermodynamically stable liquids at room temperature and have not been reported to crystallize. The corresponding X-ray diffraction data at room temperature are plotted in Figure 2. In the inset of Figure 1 we also report the corresponding correlation lengths, L, for the cases [C6mim][BF$_4$] and [C8mim][BF$_4$] and these spacings are quite close to the corresponding ones obtained for the chloride-based RTILs.

These results suggest that the behavior observed for the chloride-based RTILs is confirmed for the case of the tetrafluoroborate-based RTILs, thus indicating that the observed nanoscale correlations exist both in supercooled and in liquid RTILs.

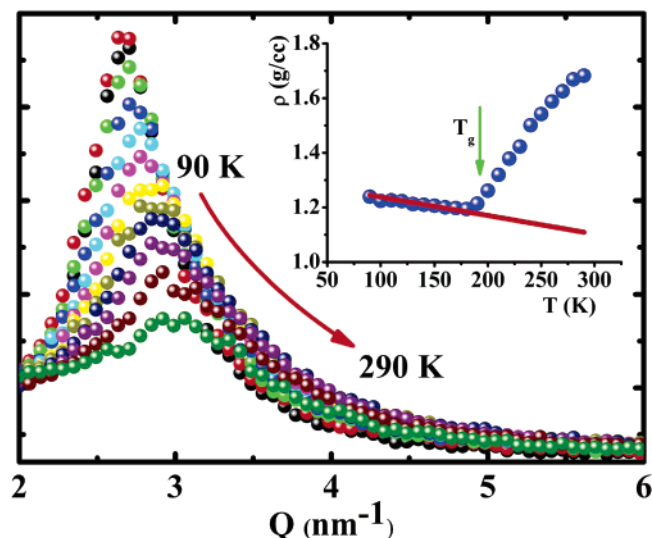We also have collected X-ray diffraction data on RTILs based

Nanoscale Segregation in RT Ionic Liquids

J. Phys. Chem. B, Vol. 111, No. 18, 2007 **4643**

Figure 3. X-ray diffraction patterns from liquid and supercooled [C8mim][BF$_4$], as a function of temperature from 90 to 290 K. The data include the liquid and glassy state ($T_g \sim 190$ K). In the inset a quantity proportional to $1/(2\pi/Q_{MAX})$,[3] Q_{MAX} being the interference peak position, is compared to the extrapolation in the low-temperature region of the experimental data for the density of [C8mim][BF$_4$].[22]

on other anions and the same qualitative behavior is observed: RTILs possessing intermediate alkyl chain lengths are characterized by the existence of a substantial degree of intermediate range order whose spatial extent is proportional to the alkyl chain length.

To get further insight into the morphological details of liquid and supercooled RTILs, we have explored the temperature dependence of the X-ray diffraction pattern from selected RTILs. In Figure 3, the data for [C8mim][BF$_4$] are reported for selected temperatures in the range 90−290 K. One can appreciate a distinct temperature dependence for the X-ray diffraction pattern: upon decreasing the temperature the interference peak shifts to lower Q values, indicating an increasing of the corresponding spatial correlation size, L. This behavior is at odds with the expectation on the basis of the temperature dependence of the density. In the inset of Figure 3 the temperature dependence of ρ^* ($=\alpha/(2\pi/Q_{MAX})$,[3] where α is a scaling term that is chosen to facilitate comparison with density data, is plotted. This data set is compared with the extrapolation of the temperature dependence of the density of [C8mim][BF$_4$], reported by Harris et al.[25] that was determined in the range 273− 363 K. The extrapolation of the temperature dependence of the density to the below-T_g range (where $T_g \sim 190$ K) nicely accounts for the peak position shift observed in this temperature range. On the other hand, in the high-temperature range, between room temperature and the glass transition, the interference peak shifts following a behavior that strongly deviates from the density one. Such evidence would indicate that the mechanism responsible for the temperature dependence of the spatial correlation growth with decreasing temperature is related to diffusion: as long as diffusive processes get arrested (i.e., below T_g), the spatial correlation does not grow any longer and its size is only determined by the density changes.

The scenario emerging from this experimental evidence is quite complex and can be rationalized considering that in the explored temperature range those RTILs which are characterized by an alkyl chain length $n \geq 4$ show a distinct degree of intermediate range order, in agreement with the proposals suggested on the basis of MD simulations.[19−22] This structural correlation is the consequence of the aggregation of the alkyl

tails; such a process occurs embedded in a polar environment that is built up by the anion and the charged imidazolium rings: as a consequence of the strong and isotropic Coulombic interactions, MD simulations propose a structurally homogeneous matrix built up by the charged portions of the RTIL. The short range, collective interactions between the uncharged alkyl chains then lead to quite stable segregated domains.

MD simulations also propose that above a certain temperature, T_c, these alkyl domains will melt.[22] Though these simulations were run using a unrealistic potential[22] to describe the precise details of the RTIL architecture, still they get the essence of the phenomenology.

Our measurements were not conducted at sufficiently high temperature to observe any effect that might be related to the melting of the domains, but some indications exist in the literature for such a process. In their report on the thermodynamic properties of [C4mim][PF$_6$], Kabo et al.[26] observed an endothermic contribution between 400 and 420 K. We repeated DSC measurements on this RTIL in our laboratory and confirmed these findings. These observations refer to a liquid sample and, though one cannot exclude to relate it to the effect of a small amount of residual water dispersed in the sample, it might as well be related to the *melting* of the nanoscale domains in [C4mim][PF$_6$]. Similarly, Hamaguchi and co-workers[27,28] interpreted the very long thermal equilibration of [C4mim]Cl at 110 °C as due to the existence of "some local structures" in the liquid RTIL. These findings support the scenario of a phase transition from the solid nanodomains to the homogeneous liquid.

Conclusion

Neat room-temperature ionic liquids based on alkyl imidazolium cations with intermediate length for the alkyl tail ($4 \leq n \leq 10$) have been shown, by means of X-ray diffraction, to be characterized by the existence of structural organization at the nanometer scale, both in their liquid and supercooled state. The characteristic size of these structural heterogeneities is found to linearly scale with the alkyl chain length, thus suggesting that these nanodomains are built up by the aggregation of neutral alkyl tails which are surrounded by charges whose uniform spatial distribution is determined by the strong electrostatic interactions.

The temperature dependence of the X-ray diffraction patterns from [C8mim][BF$_4$] shows a peculiar behavior: the interference peak that is associated with a spatial correlation of the order of 20 Å shifts with temperature. Between room temperature and T_g, the size of this spatial correlation increases with decreasing temperature. Below T_g the density-driven decreasing of the domain size is recovered upon decreasing the temperature. These observations seem to indicate that diffusive processes strongly affect the morphology of these nanodomains.

The observed morphological organization will require further detailed theoretical and experimental efforts to be fully understood and exploited. Moreover, this nano-organization is expected to lead to important effects when mixing RTILs with polar or nonpolar components and to play a major role for new applications such as smart synthesis, solutes confinement, phase equilibria, etc.

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