Structure of Aqueous Solutions of Ionic Liquid 1-Butyl-3-methylimidazolium Tetrafluoroborate by Small-Angle Neutron Scattering

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The structure of aqueous solutions of a prototype ionic liquid, the short alkyl chain 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4mim][BF_4]) has been investigated by small-angle neutron scattering. Concentration fluctuations and Kirkwood–Buff integrals have been calculated, and the results are in good agreement with corresponding data calculated herein from vapor pressure measurements. The large concentration fluctuations and Kirkwood–Buff integral values indicate that the system is in the vicinity of phase separation, which is known to occur some 20 K below room temperature, at a salt mole fraction of around 0.075.

1. Introduction

An ionic liquid is a salt composed of an organic cation and an inorganic or organic anion, which has the particularity of being in liquid state at temperatures close to room temperature. They have several unusual properties, such as negligible vapor pressure, a wide electrochemical window, nonflammability, high thermal stability, and wide liquid range.[1] For all these physicochemical properties, they are usually considered as environmentally friendly, "green" solvents.

Among ionic liquids, those based on the 1-alkyl-3-methylimidazolium cation ([$C_n$mim]) salt have recently received particular attention. A specific feature of these salts is that the alkyl chain length of the [$C_n$mim] cations can be varied through the C_n group, thus enforcing their amphiphilic character in aqueous solutions toward typical surfactants for long chains. However, not all such salts are miscible with water, and their hydrophobicity can be tuned by varying the type of anion. Thus, some salts containing a given cation are totally miscible with water (e.g., those containing the BF_4^- anion), whereas others containing the same cation are partially miscible or even immiscible (e.g., with PF_6^- anion).[2–4]

In spite of the growing interest in these green solvents, the basic rules governing their physical and chemical properties are not yet fully understood. After numerous thermodynamic and physicochemical studies,[5] it is only recently that their bulk state has started to be explored by more powerful methods, allowing one to elucidate their structure and dynamics on a microscopic scale. Diffraction studies[6,7] have revealed notable molecular organization on the nanometer length scales for all salts based on pure imidazolium that have been studied so far. This strong tendency toward enhanced local structure is what distinguishes these types of liquids from the much more homogeneous

ordinary molecular liquids.[8] Computer simulations[9,10] have shown that alkyl tails aggregate through van der Waals attraction, while the ionic head groups and the anions are distributed more homogeneously, forming a continuous network of ionic channels.

In contrast to the neat ionic salts, structural investigations of aqueous solutions of ionic liquids are still scarce. The traditional physical chemistry methods reveal a tendency toward self-aggregation of the salts, usually above a certain concentration threshold around intermediate compositions.[11–15] This threshold concentration has been referred to as the critical aggregation concentration (cac),[15] by analogy to the critical micellar concentration (cmc). This analogy has been based on similarities in the concentration dependence of the surface tension and the conductivity between solutions of conventional surfactants and aqueous ionic salts.

More detailed information on the structure of the solutions, however, can hardly be obtained from thermodynamic measurements alone. The techniques of small-angle neutron scattering (SANS) and X-ray scattering (SAXS) are rather well suited for studying surfactant solutions, since they can provide precise information on the shapes and sizes of various aggregates forming in the mixtures, having sizes of several nanometers. They are also proven to be useful for measuring the extent of association of small molecules in binary or multicomponent solutions,[16–19] or for studying critical fluctuations in molecular fluids or mixtures.[20,21]

In a recent SANS study of aqueous solutions of several alkyl-methyl-imidazolium salts, different kinds of micellar aggregates were observed in a wide range of salt concentrations.[15] The short alkyl chain salt 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4mim][BF_4]) was suggested to assemble in micelle-like aggregates, which were modeled as polydisperse spheres consisting of the salt and a substantial amount of water. For aqueous [C_8mim][I], the low-concentration solutions could be modeled by ellipsoidal micelles with repulsing interactions, while, for higher concentrations, this system developed into a well-ordered state showing a sharp diffraction peak, pointing

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to nanoscale segregation. For an even longer alkyl chain salt, [C$_{10}$mim][Br], concentration-dependent complex phase behavior has been found.[22] Increasing the salt fraction, that is, decreasing the water content, the gel-like ordering in this system evolves from lamellar to hexagonal and/or gyroid structures.[23]

While the formation of micelles or micelle-like aggregates may be plausible for ionic salts with longer alkyl tails, such micelles, in the proper sense, are not really expected for shorter chain salts, such as the presently investigated butyl-methyl-imidazolium salt. In our study, we focus on the short alkyl chain, and report a SANS investigation on the mixture [C$_4$mim][BF$_4$]—heavy water. We show that the structural data can be interpreted entirely within the framework of the statistical thermodynamics,[24] and the structure of the mixtures is dominated by statistical concentration fluctuations, instead of aggregation as suggested earlier.[15]

Such mixtures of short alkyl chain ionic salts are also interesting because one can investigate the relationship between the strong concentration fluctuations and the formation of micro-heterogeneity, without having to worry about phase transitions or phase separation behavior, which often tend to mask and obscure the local structure of aqueous solutions. Archetypical examples of both situations are aqueous acetone and aqueous acetonitrile mixtures, the latter displaying the behavior typical of a proximity of a phase separation,[16] while, in the former, the water shows extended self-association.[17] In the present case, both our pure components—the ionic liquid and water—are known to exhibit clustering tendencies, although with different underlying mechanisms. For the ionic liquid, this ordering is due to the self-attraction of the alkyl parts, while water possesses an extended hydrogen-bonded network. Their mixtures, according to our analysis, while possibly micro-heterogeneous, show large concentration fluctuations at a salt mole fraction of about $x \approx 0.075$, suggesting that the mixture might be close to phase separation. This finding agrees with recent thermodynamic results,[25] which locate the upper critical solution point at $T \approx 277$ K. We provide below our arguments for such a conclusion from analysis of the concentration fluctuations and the Kirkwood—Buff integrals (KBIs).

2. Experimental Section

SANS on solutions of [C$_4$mim][BF$_4$] in heavy water was measured on the SANS instrument *Yellow Submarine* operating at the Budapest Research Reactor. Heavy water was used as the solvent in order to increase the contrast in the scattering length densities between the two components, thus improving the precision of the experiment. The measurements were performed at 25 °C, for 11 samples covering the concentration range of 0.01—0.16 in salt mole fraction. The ionic salt was synthesized as in refs 14 and 26, and heavy water of 99.3 atom % deuterium content was used. Solutions were prepared by weighing a few hours prior to measurements. The samples were measured in 1 mm-thick quartz cells, and the counting times were between 40 and 100 min per sample. The range of scattering vectors q was set to 0.063—0.36 Å^{-1} [$q = (4\pi/\lambda) \sin \Theta$; λ is the neutron wavelength, and 2Θ is the scattering angle].

The rough scattering curves were corrected for the sample transmission, the scattering from the cell, and the room background. Correction to the detector efficiency and conversion of the measured scattering to absolute scale was performed by normalizing the spectra to the scattering from a light water sample. After the corrections, the statistical error of the data
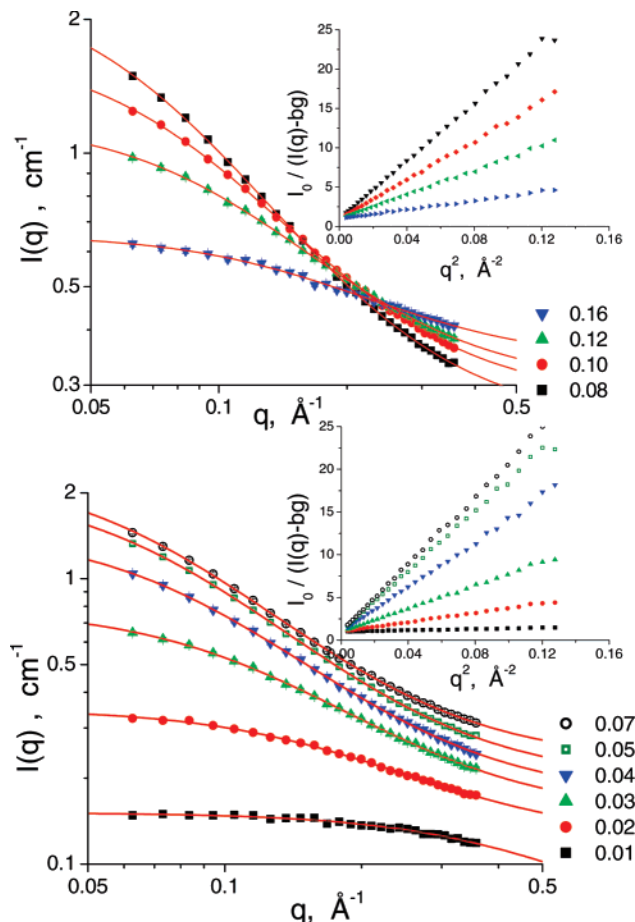

Figure 1. SANS scattering curves of aqueous solutions of ionic salt [C$_4$mim][BF$_4$] measured at 25 °C. Mole fraction of salt is indicated. The lines are fits to eq 1. Insets show the same data represented in Ornstein—Zernike-type plots.

points of the spectra was around 1%, and the uncertainty of converting the scattering intensity to absolute scale was about 5%.

3. SANS Results

The scattering curves for the mixtures are shown in Figure 1, together with the least-squares fits to the Ornstein—Zernike form for the statistical concentration fluctuations.[27] The corresponding scattering function is given by eq 1:

$$I(q) = \frac{I_0}{1 + q^2\xi^2} + Bg \tag{1}$$

where I_0 is the coherent forward scattering intensity, ξ is the correlation length, which is the measure of the decay of the density—density correlations, and Bg is a flat background term. The latter accounts for the contribution of the incoherent scattering from the hydrogen and deuterium atoms in the mixture.

A nice agreement is seen between the experimental data and the Ornstein—Zernike behavior for all spectra, over the entire studied concentration range. This suggests that the distribution of the molecular species in the system is similar to the case of strong concentration fluctuations. The forward scattering intensities and the correlation lengths are displayed in Figure 2, and the results of fitting are collected in Table 1. Both quantities show maxima at a salt mole fraction of about 0.07, and their
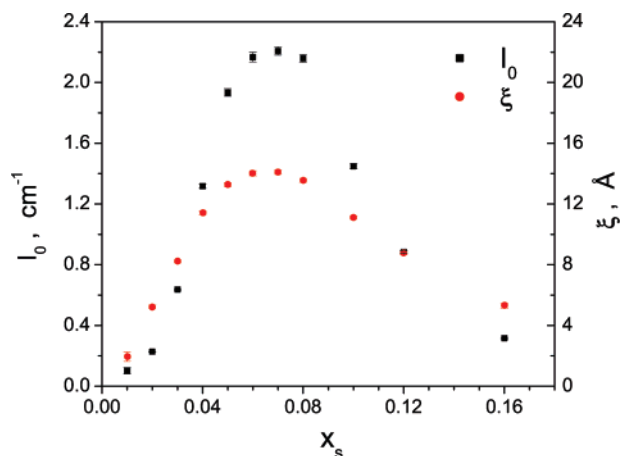
Figure 2. The coherent forward scattering intensity and the correlation length as determined by fitting eq 1.

behavior is rather characteristic for binary mixtures of molecular fluids having strong concentration fluctuations.[16,28,29]

Using the values of forward scattering intensity, several thermodynamic quantities were calculated, such as the values of concentration fluctuations, that are related to the thermodynamic "*D*" parameter and the Kirkwood−Buff integrals, as described in the following section.

4. Concentration Fluctuations and KBIs

Density and concentration fluctuations in a two-component system with N_i particles for species i ($i = 1,2$) are simply given by the following statistical averages:[30,31]

$$S_{ij}(0) = \langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle$$

$$S_{CC}(0) = x_2^2 S_{11}(0) + x_1^2 S_{22}(0) - 2x_1 x_2 S_{12}(0) \quad (2)$$

where $S_{CC}(0)$ is the zero wave vector value of the concentration−concentration structure factor, x_i is the mole fraction of species i, and the average is generally performed in the grand canonical ensemble, which allows for fluctuations of the number of particles. These concentration fluctuations in mixtures can be measured in two different ways. Statistical mechanics relate $S_{CC}(0)$ to the first-order mole fraction partial derivatives of the chemical potentials,[24] as well as to the partial structure factors.[24,32] Therefore, these two routes should be equivalent ways to compute the concentration fluctuations from different experiments.

Concentration Fluctuations from Vapor Pressure Measurements. The vapor pressure study of this particular aqueous ionic liquid has been performed recently by Koga and co-workers.[33] The excess chemical potentials for water μ_w^E and the salt μ_s^E have been calculated from the measured pressure and equally reported in ref 33. These quantities are indispensable for a direct computation of the concentration fluctuations that are related[24] to the inverse of the mole fraction derivatives ($\partial \mu_i / \partial \langle N_j \rangle)_{T,P,\mu_k}$, where $i = $ w, s, and the derivative is performed at constant temperature T, pressure P, and chemical potential of all other species.

In our case of a binary mixture, the derivatives are then interrelated, and any one of them is enough to compute the concentration fluctuations.[18] Since the experimental chemical potentials are provided numerically, the derivatives can also be taken numerically; the appropriate procedure to extract the concentration fluctuations has been outlined in ref 18 and applied here. Here, we recall the procedure. First, the two excess

chemical potentials are differentiated numerically with respect to the solute mole fraction. The needed derivative is then visually fitted to match the average between the two derivatives. These total and excess chemical potentials are shown in Figure 3. Since this procedure is numerical, it can be justified by success of the direct comparison with the equivalent data as produced by SANS experiments.

Concentration Fluctuations from SANS. The forward scattering intensity measured by SANS is related to the magnitude of the concentration fluctuations and to KBIs.[32,34] $S_{CC}(0)$ can be calculated from the forward scattering intensity and the partial molar volumes of the components:

$$S_{CC}(0) = \frac{I_0 + \rho x_s x_w (b_s - b_w)^2}{\rho [\bar{b} \delta - (b_s - b_w)]^2} \quad (3)$$

where I_0 is the q-dependent coherent forward scattering intensity (see eq 1), ρ is the number density of the molecules, b_s and b_w are the sums of the coherent scattering lengths of the nuclei in molecules of the ionic salt and the heavy water, respectively, $\bar{b} = x_s b_s + x_w b_w$, $\delta = (V_s - V_w)/V_{mol}$ is the dilatation factor, V_s and V_w are the partial molar volumes of the components, and V_{mol} is the molar volume of the mixture. Here the ionic salt is treated as one species. Molar volumes and partial molar volumes have been determined by density measurements on light water solutions of the ionic salt.[35]

Now, we can compare the concentration fluctuations obtained from the two routes. Before, we showed in Figure 3 the total and excess chemical potentials from ref 33 for our binary system, as a function of the mole fraction of the solute. It is noteworthy to mention that we have been able to numerically complement the excess chemical potential of salt at low mole fraction from ref 33 by imposing the constraint that the fluctuations calculated from the chemical potentials of both components should be equal.

The concentration fluctuations are shown in Figure 4 in their two different representations (the direct and the inverse forms), the latter being $D = x(1 - x)/S_{CC}(0)$, which appears in the original expressions of the KBIs. One sees that the agreement of the two *independent* methods is nearly perfect, as it should be if everything is done properly. Namely, the positions of the extrema are located at about $x \approx 0.075$ for both data sets. The position of the extrema at a low mole fraction of the salt is due to the large size of the solute molecule compared to the water molecule. We also observe that the minimum in D is very close to zero, which means that the fluctuations are very strong as if they could induce a phase separation. Indeed, the condition $D = 0$ corresponds exactly to the spinodal condition of phase separation.[31] However, the actual proximity of the minima does not tell how far in temperature is the system close to the demixing region, which is known to be below $T = 278$ and 281 K for light and heavy water mixtures, respectively.[25] The occurrence of concentration fluctuations is certainly related to the strong micro-heterogeneous structure this type of mixture is supposed to exhibit, on the basis of the fact that the cation has a hydrophobic tail.[10] However, the analysis of the present report and that of Bowers et al.[15] indicates that the issue about how the concentration fluctuations and the micro-heterogeneity contribute to the small q behavior of the scattering intensity is a fundamental one for our comprehension of the local structure of these complex mixtures. What is clear from these results is rather that the fluctuations are very strong, which is probably due to the proximity of a demixing transition. The ideal mixing behavior of the concentration fluctuations, namely, $S_{CC}(0) =$

TABLE 1: Results of Fitting of Eq 1 to the SANS Data of [C₄mim][BF₄]−D₂O Mixtures, and the Calculated Concentration Fluctuations at $T = 25\ °C^a$

x_s	c (mmol dm⁻³)	I_0 (cm⁻¹)	ξ (Å)	Bg (cm⁻¹)	S_{CC}
0.01	504	0.101 ± 0.021	1.95 ± 0.32	0.050 ± 0.022	0.017 ± 0.005
0.02	926	0.228 ± 0.002	5.24 ± 0.10	0.122 ± 0.002	0.048 ± 0.003
0.03	1290	0.636 ± 0.005	8.22 ± 0.09	0.149 ± 0.001	0.167 ± 0.010
0.04	1600	1.317 ± 0.016	11.43 ± 0.13	0.171 ± 0.001	0.428 ± 0.026
0.05	1870	1.934 ± 0.025	13.27 ± 0.14	0.196 ± 0.001	0.761 ± 0.047
0.06	2110	2.167 ± 0.032	14.02 ± 0.16	0.212 ± 0.001	1.029 ± 0.067
0.07	2320	2.208 ± 0.028	14.10 ± 0.14	0.229 ± 0.001	1.249 ± 0.076
0.08	2510	2.158 ± 0.025	13.56 ± 0.12	0.246 ± 0.001	1.436 ± 0.089
0.10	2830	1.448 ± 0.015	11.11 ± 0.11	0.279 ± 0.001	1.314 ± 0.079
0.12	3100	0.884 ± 0.008	8.76 ± 0.10	0.302 ± 0.002	1.061 ± 0.062
0.16	3510	0.316 ± 0.003	5.32 ± 0.16	0.340 ± 0.004	0.624 ± 0.034

^{a} The molar scale refers to solutions of [C₄mim][BF₄] in light water, and corresponds to densities measured in ref 35.
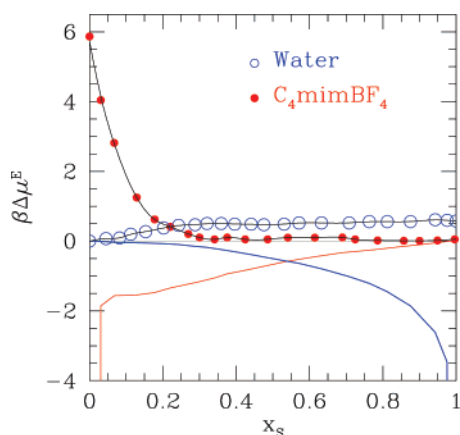
Figure 3. Excess chemical potentials (circles) and total chemical potentials (lines) for [C₄mim][BF₄] at 25 °C (ref 33, see text).

$x(1 - x)$, is shown by a dashed line in the top panel of Figure 4. It is seen that it merges quite nicely at high salt mole fractions with the data from the vapor pressure measurements, thus suggesting the possible ideality of the mixture in the salt mole fraction range of 0.4−1.

Kirkwood−Buff Integrals. The KBIs (G_{ij}) are defined (see, e.g., ref 24) in terms of the molecular pair correlation functions ($g_{ij}(r)$) between the species i and j:

$$G_{ij} = \int_0^\infty (g_{ij}(r) - 1)4\pi r^2 dr \qquad (4)$$

The statistical mechanical interpretation of these quantities is in terms of concentration fluctuations, and they are related to thermodynamic quantities such as the compressibility, partial volumes, and chemical potentials.[24,32,31]

The KBIs can be directly calculated from the concentration fluctuations, partial molar volumes and the isothermal compressibility.[24,32] The compressibility of these mixtures is not known to date. Since they do not have much affect on the resulting KBIs, we have replaced these values by compressibility of water. The experimental KBIs for [C₄mim][BF₄]−D₂O mixtures are shown in Figure 5. The data from the thermodynamical route have been plotted for two sets of volumes. The open symbols with blue lines are for the correct partial molar volumes as computed from the high quality experimental data, while the red lines (barely visible) are for the *constant* partial molar volumes equal to the volume of the respective pure components. Such simplification is seen to make no difference to the results, just as has been shown also for alcohol−water mixtures.[18] The first remark is regarding the rather large KBIs that are obtained near the extrema mole fraction $x \approx 0.075$.
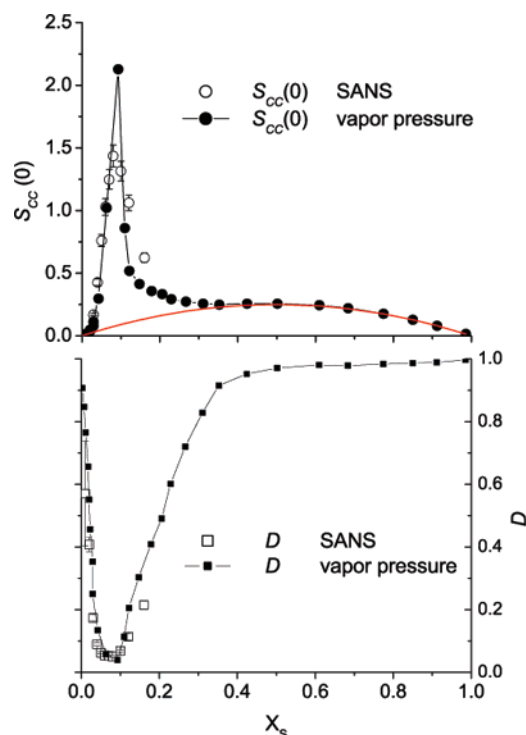
Figure 4. Concentration fluctuations (top panel) and D factor (lower panel) for aqueous solutions of [C₄mim][BF₄] at 25 °C. Filled symbols are for the thermodynamical route, and open symbols are for the SANS data. Solid red line shows concentration fluctuations for an ideal system.

This is in accord with the proximity of a phase demixing that happens just 20 degrees lower.[25] Next, we observe that the agreement between the SANS and thermodynamical route presents a lesser accuracy than that observed for fluctuations in Figure 4. The reason for this disagreement comes from the fact that the small discrepancies that are barely observable in Figure 4 are now amplified, especially near $x_s \approx 0.075$, because of the small values of D. Nevertheless, the agreement is quite remarkable, and better than most data where such a direct comparison is provided in the literature.[36,37]

5. Discussion

Scattering data can, in general, be interpreted differently for two broad categories of liquids, simple atomic and molecular liquids, and colloidal liquids. In both cases, the scattering intensity can be written as $I(q) \propto P(q)S(q)$, but the two functions will be different for the two cases. This decomposition is naturally made for molecular liquids and their mixtures, for which $P(q)$ is given by the interatomic distances in the molecule,
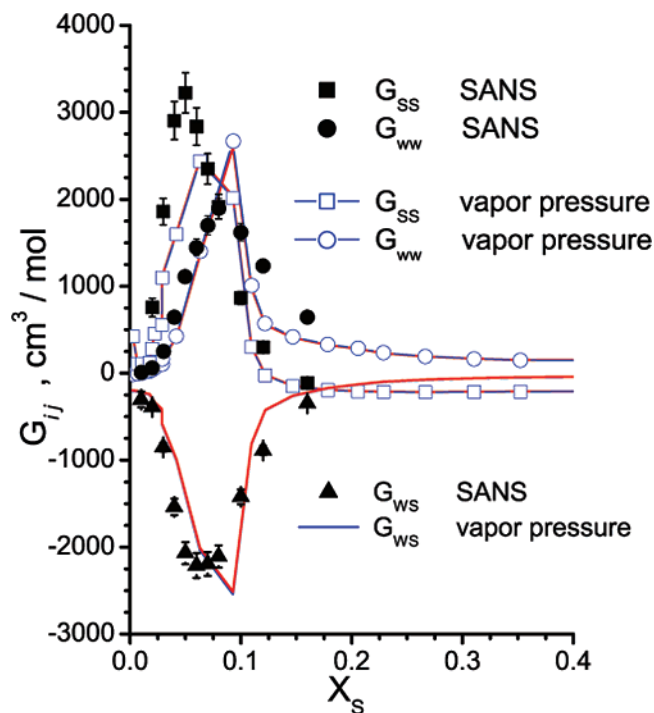
Figure 5. KBIs (G_{ij}) in aqueous solutions of [C$_4$mim][BF$_4$] at 25 °C, calculated from SANS and vapor pressure data. The blue and red lines are for different definitions of the partial molar volumes (see text).

and $S(q)$ is the liquid structure factor, reflecting the distribution of the molecules. The same decomposition can also be made for a higher structural level corresponding to colloidal particles, such as micelles or macromolecules, in which case $P(q)$ will correspond to the shape of the micelles and $S(q)$ will characterize their spatial distribution.

When the separation in scale between micelles and molecules becomes blurred, that is when molecules form aggregates that are not quite micelles yet, then the interpretation in terms of form and structure factors for micelles becomes difficult. However, in all cases, the small-q behavior of the liquid structure factor $S(q)$ reveals the state of the concentration fluctuations in the mixture, which is an exact result from statistical mechanics.[30,31] In our choice, we do not impose the existence of any aggregates, but use the molecular level form factor and the liquid structure factor. Doing so, we avoid the overlapping effects of the fluctuations and micellar form factor, which may act in the same range of q. At present, there is no clear-cut way of deciding which method is appropriate since both methods involve approximations in the interpretation of the small-q behavior, either for the form factor of the micelles or for the liquid structure factor.

Using this approach, we are able to fit perfectly the scattering intensities of this system to the Ornstein−Zernike form of statistical concentration fluctuations over the whole concentration range studied, which is a smaller use of fitting parameters, when compared to the multiparameter fits necessary for describing micelles.[15] The principle of economy in the number of fitting parameters, as well as the quantitative agreement between the fluctuations obtained by SANS and calculated independently from vapor pressure data, gives further support to the validity of the used approach.

The behavior of all the measured and calculated quantities is similar to that of many other binary aqueous solutions that show highly nonideal mixing.[16,29] Although the intermolecular interactions responsible for the microscopic demixing are not identified from the structural data obtained in the experiment, the presented

results allow one to place the aqueous solutions of short-chain ionic liquids into the general family of systems with nonideal mixing behavior. The high KBIs obtained suggest strongly that the system is quite close to a demixing spinodal at a mole fraction of about $x_s \approx 0.075$. The main reason to conclude this is the fact that all three G_{ij} values are large at $x_s \approx 0.075$, a direct consequence of the smallness of D at this composition. This is similar to the case of aqueous acetonitrile, where such behavior is equally observed with high magnitude of all three G_{ij} values, together with the existence of an underlying upper critical solution temperature (UCST) some 25 °C below room temperature.[16,28] The fact that two different cosolvents, namely, acetonitrile and ionic salt, give very similar behavior further enforces the thesis of precritical fluctuations, mainly in view of the universality of this latter phenomena.

Analysis of the vapor pressure data in terms of second derivatives, introduced by Koga,[38] reveals a critical concentration of about 0.015, denoted as a transition between mixing schemes.[33] Analogous transition is found for this system by surface tension measurements.[14,15] While these thermodynamic results are indicative of some sort of possible structural transition occurring at this concentration, they are not informative on the nature of these structural changes. Our scattering data, as well as those of Bowers et al., show strong fluctuations, or aggregation above this point. The nature of the underlying microheterogeneity or micelle formation is unfortunately not clarified by this discussion, since it is masked by the strong precritical scattering due to concentration fluctuations inherent to this region.

6. Conclusions

Aqueous solutions of a typical ionic liquid have been studied by SANS, in the concentration range where the structural inhomogeneities are the largest. The mixtures have been well described by the Ornstein−Zernike form of statistical concentration fluctuations. This has been illustrated by determining relevant quantities, such as the magnitude of the concentration fluctuations, and the KBIs. The results indicate that the system exhibits the strongest inhomogeneity at a composition of 7−8 mole percents of the salt, which corresponds to about 0.5 in volume fraction. The absence of any particular feature at small wave vectors, as well as the high scattering intensities at zero wave vector, giving rise to small D and high KBIs at $x_s \approx 0.075$, strongly suggest that the system is close to phase separation. To conclude, the general behavior for concentration fluctuations observed for this particular aqueous ionic solution is similar to that of many aqueous mixtures brought in the vicinity of demixing conditions.

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