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Chemical Potentials in Aqueous Solutions of Some Ionic Liquids with the 1-Ethyl-3-methylimidazolium Cation

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We determined the vapor pressures of aqueous solutions of 1-ethyl-3-methylimidazolium ([C₂mim])⁺-based ionic liquids (IL) with counteranions, tetrafluoroborate (BF₄⁻), trifluoromethanesulfonate (OTF⁻), and iodide (I⁻). Because in literature the evidence is accumulating and pointing to the fact that ionic liquid ions do not dissociate in aqueous media for the most of the concentration range, we analyzed the vapor pressure data on the basis of binary mixture, and the excess chemical potentials of each component were calculated. From these, the intermolecular interactions in terms of excess chemical potential and hence the concentration fluctuations were evaluated. Though any further discussion into the mixing schemes of the mixture awaits the excess partial molar enthalpy and hence the excess partial molar entropy data, the net interaction in terms of excess chemical potential indicates that the affinity of each IL is ranked in the descending order [C₂mim]I > [C₂mim]OTF > [C₂mim]BF₄. This is consistent with our earlier findings that [C₂mim]⁺ is modestly amphiphilic with almost equal hydrophobicity and hydrophilicity, I⁻ is a hydrophile, and OTF⁻ is amphiphilic, and BF₄⁻ is believed to be strongly hydrophobic.

Introduction

We have earlier studied aqueous solutions of ionic liquids (abbreviated as IL) with the 1-butyl-3-methylimidazolium ([C₄mim])⁺ cation^{1–3} by a differential approach in solution thermodynamics.⁴ Here we report the excess chemical potentials in aqueous solutions of three 1-ethyl-3-methylimidazolium ([C₂mim])⁺-based ionic liquids with tetrafluoroborate (BF₄⁻), trifluoromethanesulfonate (OTF⁻), and iodide (I⁻) anions. A fuller study will follow in due course after determining the excess partial molar enthalpies, and hence entropies as we did earlier with some [C₄mim]ILs.^{1–3} We suggested in those studies that in aqueous solutions of [C₄mim]BF₄ and [C₄mim]I, the constituent ions are completely dissociated only in the very H₂O-rich region, $x_{\text{IL}} < 0.013$ – 0.015 , where x_{IL} is the mole fraction of IL. Above this threshold, counterions begin to associate together probably via H₂O and eventually in the range $x_{\text{IL}} > 0.6$, IL molecules appear to cluster in a similar manner as in the pure state.^{1,2} The first threshold $x_{\text{IL}} \approx 0.014$ is consistent with the so-called “critical aggregation concentration” (CAC) in the literature for [C₄mim]BF₄–H₂O by NMR,⁵ conductivity,^{6,7} small angle neutron scattering,⁶ and surface tension⁶ studies. The NMR study also indicated the same value of CAC for [C₄mim]Cl–H₂O.⁵ A more recent NMR study for [C₄mim]Br–D₂O, however, gave the value of CAC $x_{\text{IL}} \approx 0.04$.⁸ Another recent NMR study using the so-called bipolar pulse pair stimulated echo method indicated there is an anomalous dynamic behavior below $x_{\text{IL}} \approx 0.0019$.⁹ As for the change in mixing

scheme at about $x_{\text{IL}} = 0.6$ for [C₄mim]BF₄–H₂O, there is a recent support by IR-Raman spectroscopic study.¹⁰

All the above studies concentrate on IL's with $k \geq 4$ in [C_kmim], and there seems to be no information available in the literature regarding ion pairing or critical aggregation for aqueous solutions of [C₂mim] counterparts. A recent study on the [C₂mim]BF₄–D₂O system using the two-dimensional correlation spectroscopy aided by density functional calculations suggested that in the range $0.1 < x_{\text{IL}} < 0.98$ the IL ions do not dissociate.¹¹ Thus, except for a very H₂O-rich region, the IL–H₂O systems could be regarded as a binary mixture; IL and H₂O, rather than a ternary mixture of IL cation, IL anion and H₂O.

We determine chemical potentials by measuring vapor pressure isothermally using a static method described at some length elsewhere.^{12,13} Briefly, we change the composition of the liquid phase sample transferring volatile component (H₂O in the present case) quantitatively in a vacuum system, and measure the total pressure of the head space over the liquid mixture. This method is more convenient than ebulliometry (in which the liquid phase composition is fixed and the boiling point vs the total pressure is determined) commonly used for a number of IL–H₂O systems.^{14–16}

Experimental Section

[C₂mim]BF₄ (95%, Kanto Chemicals) and [C₂mim]OTF (98%, Tokyo Chemicals Ind.) were used as supplied. [C₂mim]I was synthesized and purified.¹⁷ The resulting colorless crystal was dissolved in CD₃CN and was subjected to ¹H- and ¹³C-NMR analysis using JNM-LA 400s spectrometer, JEOL. No impurity other than H₂O was detected. For H₂O, all samples used were evacuated for 3 days to 10^{−6} Torr. Although the former two are liquid, the latter is solid at room temperature.

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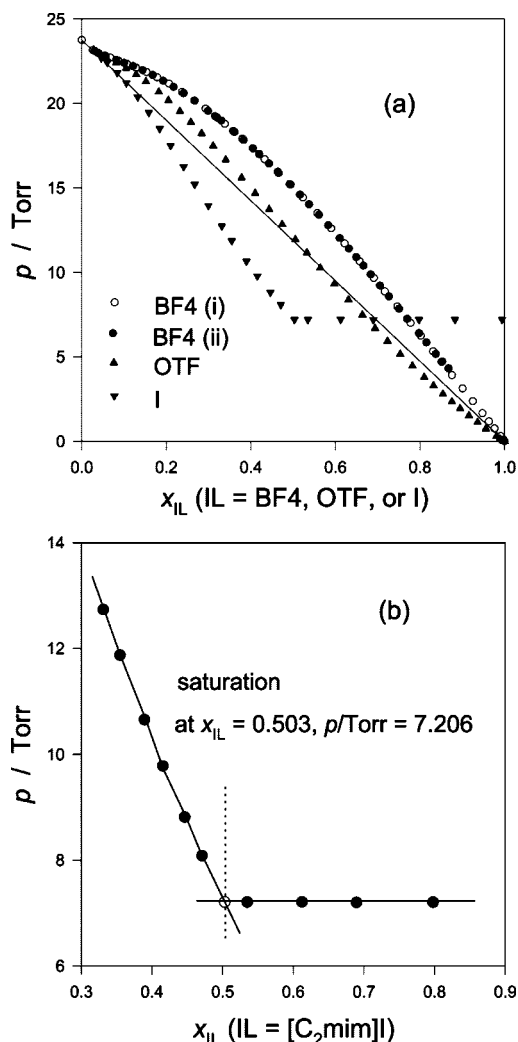


Figure 1. (a) Vapor pressure of IL–H₂O at 25 °C. IL = [C₂mim]BF₄ (BF4), [C₂mim]OTF (OTF), or [C₂mim]I (I). For BF4, there are two series of measurement, from the data of which the uncertainty of p was estimated as ± 0.006 Torr. See text. (b) Vapor pressure of [C₂mim]I–H₂O at 25 °C near the saturation point.

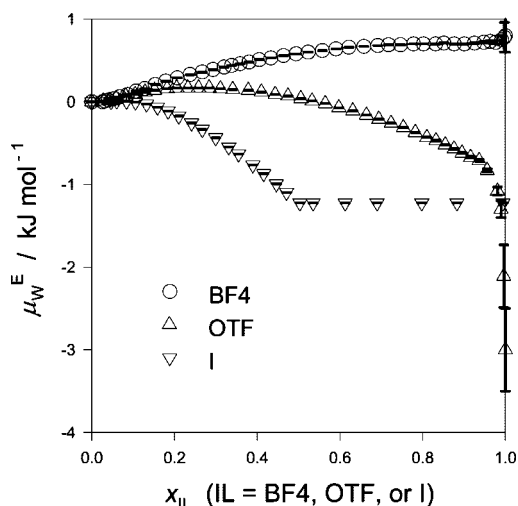


Figure 2. Excess chemical potential of H₂O, μ_W^E , in IL–H₂O at 25 °C. IL = BF4, OTF, or I.

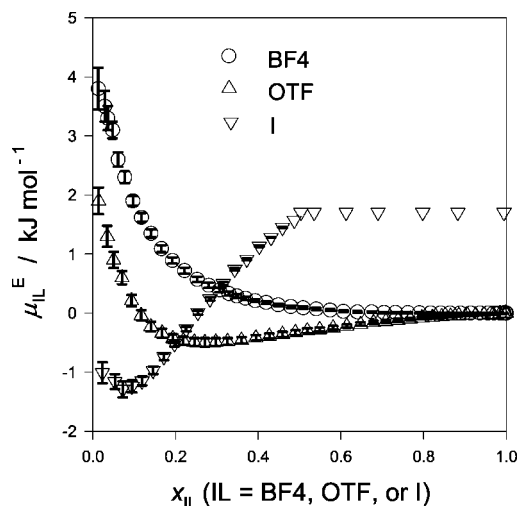


Figure 3. Excess chemical potential of IL, μ_{IL}^E , in IL–H₂O at 25 °C. IL = BF4, OTF, or I.

vacuum distilled prior to use. Vapor pressures were determined by a homemade apparatus.^{12,13,22} The sample IL was placed in the cell in the vacuum system, and evacuated for 3 days to 10^{-6} Torr, as mentioned above. The vapor pressure over the sample after this treatment was found zero within the sensitivity (± 0.001 Torr) of the capacitance manometer used (MKS, Baratron Gauge, 220DD). An amount of H₂O was vacuum transferred from the manifold with a known volume, temperature and pressure determined by the same gauge. The amount of H₂O transferred was calculated using the second virial coefficient of H₂O. The temperature of the cell was controlled within ± 0.001 K. After thermal equilibration, the head space pressure was determined by the same pressure gauge. We allowed 1 h for the system to reach equilibrium. Though the sensitivity of the gauge is ± 0.001 Torr, the overall uncertainty of the resulting total vapor pressure was estimated as ± 0.006 Torr, as discussed below. The BF₄[−] ion is known to undergo hydrolysis in aqueous solution, its degree depending on pH, temperature and the identity of the counteranion.²³ However, the dehydrated specimen of [C₂mim]BF₄ before and after vapor pressure measurements showed exactly the same spectrum by laser Raman spectroscopy (Hololab, 5000, Kaiser Optical Systems).

Results and Discussion

Excess Chemical Potentials of H₂O and IL. The total vapor pressure, p , are listed in the Supporting Information and plotted in Figure 1a. For convenience, we abbreviate [C₂mim]BF₄ as “BF4”, and [C₂mim]OTF as “OTF”, [C₂mim]I as “I”, and H₂O as “W” hereinafter. For BF4–W, we have made duplicate measurements BF4(i)–W and BF4(ii)–W as plotted in the figure. The uncertainty arising from temperature fluctuation ± 0.001 K will be of the same order of the sensitivity of the capacitance manometer. However, there are some other sources of causing uncertainty; thermal equilibration time for example. In comparison of the two series of measurements shown for BF4–W, we estimate the overall uncertainty in p to be ± 0.006 Torr. For I–W, we observed the liquid mixture–solid phase separation. Figure 1b shows the plots of p vs x_{IL} near the saturation point. From the intersection of extrapolation before and after the saturation, its locus was determined to be at $x_{IL}(\text{sat}) = 0.503 \pm 0.002$, and the coexistent vapor pressure $p(\text{sat}) = 7.206 \pm 0.006$ Torr, constant within the above estimate of the uncertainty in p up to $x_{IL} = 0.883$. We thus suggest that the

Melting points are reported to be 12.9 °C¹⁸ and 14.42 °C¹⁹ for [C₂mim]BF₄. Those of [C₂mim]OTF, and [C₂mim]I are -7.1 °C²⁰ and 77.4 °C,²¹ respectively. H₂O (Wako Chemicals) was

equilibrium solid is the pure [C₂mim]I. To the best of our knowledge, there is no solubility value available in the literature. At the highest mole fraction studied, $x_{\text{IL}} = 0.993$, the equilibration dynamics was found to be extremely slow with a half-life of a few days. We therefore obtain the equilibrium vapor pressure at the infinite time to be 7.0 ± 0.5 Torr by a novel numerical extrapolation technique devised by Tozaki.²⁴ We thus ensure ourselves for the above conclusion that the equilibrium solid is the pure anhydrous [C₂mim]I.

In calculating the chemical potentials, we adopt the symmetric reference system. Namely, we take the pure liquid H₂O and the pure IL at 25 °C as the reference states. Accordingly, the chemical potential of the i th component, μ_i , at 25 °C is written as

$$\mu_i = \mu_i^* + RT \ln(x_i) + \mu_i^E \quad (1)$$

where μ_i^* is the chemical potential of the pure component i , x_i is its mole fraction, and μ_i^E is its excess chemical potential containing all the information about the intermolecular interactions in the mixture. Assuming that the gas phase nonideality is negligible in comparison with that in the liquid phase, μ_i^E is written as^{12,13}

$$\mu_i^E = RT \ln\left(\frac{p_i}{p_i^* x_i}\right) \quad (2)$$

where p_i is the partial pressure of i in the equilibrium gas phase, p_i^* is the equilibrium vapor pressure of pure i . As discussed in the Introduction, the IL–H₂O systems in question can be safely regarded as binary mixtures, IL and H₂O, except for a very dilute region. Hence, $x_i = n_i/(n_W + n_{\text{IL}})$, where n_i is the molar amount of i for $i = \text{IL}$ or W . Because it is safe to assume that the partial pressure of IL is negligibly small in comparison with that of H₂O in the mixture, the measured total pressure is equal to p_W within the sensitivity of the Baratron gauge, ± 0.001 Torr. The excess chemical potentials of H₂O, μ_W^E , are calculated by eq 2. The results are listed in the Supporting Information and plotted in Figure 2. The main source of uncertainty comes from that of p_W , ± 0.006 Torr, in eq 2, and the resulting uncertainties are also listed in the Supporting Information, and shown with error bars in the figure. The excess chemical potentials of the other component IL, μ_{IL}^E , is evaluated by the Gibbs–Duhem relation,

$$x_{\text{IL}} \delta \mu_{\text{IL}}^E + x_W \delta \mu_W^E = 0 \quad (3)$$

If the value of μ_{IL}^E is known at one point, the deference $\delta \mu_{\text{IL}}^E$ is calculated for the next data point, using the change in the known value of μ_W^E . Because we adopt the symmetric reference system, $\mu_{\text{IL}}^E = 0$ at $x_{\text{IL}} = 1$, and we start at this point and calculate μ_{IL}^E stepwise. For [C₂mim]I–H₂O, at the saturation point, $x_{\text{IL}}(\text{sat}) = 0.503$, the chemical potential of liquid mixture is at equilibrium with the pure solid, μ_{IL}^* . Hence, eq 1 leads at $x_{\text{IL}}(\text{sat})$ to the relation

$$\mu_{\text{IL}}^E(\text{sat}) = -RT \ln(x_{\text{IL}}(\text{sat})) \quad (4)$$

Hence, for I–W we started the stepwise calculation at the saturation point. Using the uncertainties for each μ_W^E , the resulting uncertainty in the values of μ_{IL}^E are calculated, listed in the Supporting Information and shown in Figure 3. The determined values of x_{IL} have at least four significant figures, and its contribution to error was ignored. The uncertainty in $x_{\text{IL}}(\text{sat})$ for I–W, ± 0.002 , was taken into account.

These chemical potential data are useful in that when the excess partial molar enthalpy of i , H_i^E , becomes available, the excess partial molar entropy, S_i^E , can be obtained and with these

latter data set the detailed mixing scheme could be elucidated, as we did for the case of aqueous solutions of [C₄mim]-based IL's.^{1–3} Nevertheless, the chemical potential data alone shown in Figures 2 and 3 show a general trend in the net affinity toward H₂O of each of three ILs studied here. The [C₂mim] cation being equal, BF₄[−] is expected to be hydrophobic, whereas OTF[−] shows an amphiphilic propensity and I[−] is almost purely a hydrophile. The properties toward H₂O of the latter two anions were experimentally shown by our earlier studies.^{3,25} Accordingly, both μ_W^E and μ_{IL}^E are expected to be more positive in the order of BF₄ > OTF > I, which is the case shown in Figures 2 and 3.

Interactions in Terms of Chemical Potential. We have defined the interaction function in terms of chemical potential as^{26,27}

$$\mu_{i-j}^E = N \left(\frac{\partial \mu_i^E}{\partial n_j} \right) = (1 - x_j) \left(\frac{\partial \mu_i^E}{\partial x_j} \right) \quad (5)$$

This quantity is the effect of additional j th component on the excess chemical potential of the existing i th component. Thus, it signifies the i – j interaction in terms of net excess chemical potential. It contains the enthalpy and entropy terms, which often tend to compensate with each other.^{28,29} Thus, the detailed information about the i – j interaction should be more conspicuous in the enthalpy and entropy terms. Nevertheless, μ_{i-j}^E shows the net effect in terms of excess chemical potential.

Here we calculate $\mu_{\text{W-W}}^E$ first by eq 5 with $i = j = \text{W}$. We approximate the partial derivative of the far right of eq 5 by the slope of the cord connecting every fourth data points of μ_W^E vs x_W . The results are listed in the Supporting Information and plotted in Figure 4a. The same using closer two data points increases the size of error bars and the results scatter widely. Choosing, on the other hand, two points wider apart would introduce systematic errors in that the slope of a long cord would be different from the slope of the tangent at the mid point. Judging from the smoothness of the curve and the size of the error bars, our choice seems to be reasonable. From the Gibbs–Duhem relation, it is elementary to draw the following relations,

$$\mu_{\text{IL-IL}}^E = (x_W/x_{\text{IL}})^2 \mu_{\text{W-W}}^E \quad (6)$$

$$\mu_{\text{IL-W}}^E = -(x_W/x_{\text{IL}}) \mu_{\text{W-W}}^E \quad (7)$$

The resulting $\mu_{\text{IL-IL}}^E$ and $\mu_{\text{IL-W}}^E$ are listed in the Supporting Information and shown in Figure 4b,c. Assuming that the uncertainty in x_{IL} is negligible, the relative uncertainty remains the same as that for $\mu_{\text{W-W}}^E$, Figure 4a. This route of using the relations, eqs 6 and 7, in obtaining the $\mu_{\text{IL-IL}}^E$ and $\mu_{\text{IL-W}}^E$ data is more advantageous than using the μ_{IL}^E data and taking derivatives numerically. The latter route provides much larger error bars, because the original μ_{IL}^E data contains larger error bars to begin with than the μ_W^E data.

In Figure 4a, possible changes in mixing scheme discussed in the Introduction are not immediately obvious from the x_{IL} dependences of $\mu_{\text{W-W}}^E$, $\mu_{\text{IL-IL}}^E$, or $\mu_{\text{IL-W}}^E$. The data of the constituent enthalpy and/or entropy counterpart are awaited. As mentioned in the Introduction, we had all these data for aqueous solutions of [C₄mim]BF₄, and [C₄mim]I, which were instrumental in gaining insight into the changes in mixing scheme. Nonetheless, the general trend of each IL is evident from the figures. Figure 4c indicates that the IL–W interaction in terms of chemical potential, $\mu_{\text{IL-W}}^E$, is negative (favorable) for [C₂mim]I, and as anion changes to OTF and then to BF₄, the value of $\mu_{\text{IL-W}}^E$ becomes more positive (unfavorable) in the order

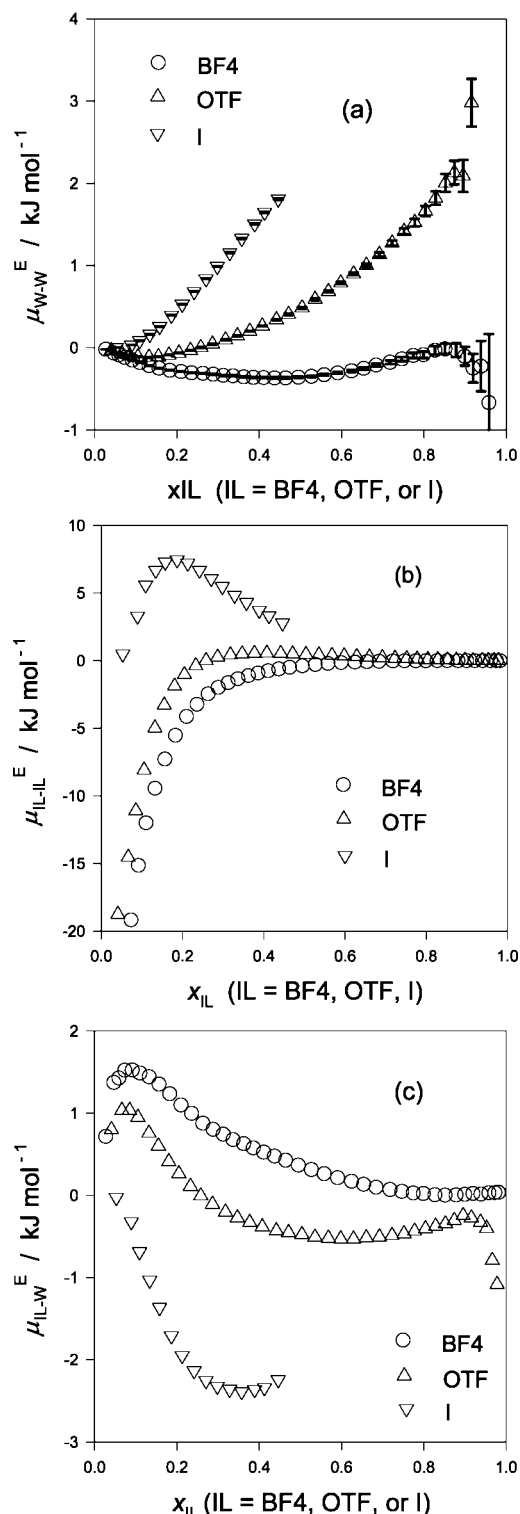


Figure 4. (a) $\text{H}_2\text{O}-\text{H}_2\text{O}$ interaction in terms of chemical potential, $\mu_{\text{W-W}}^{\text{E}}$, in IL– H_2O at 25 °C. IL = BF4, OTF, or I. (b) IL–IL interaction in terms of chemical potential, $\mu_{\text{IL-IL}}^{\text{E}}$, in IL– H_2O at 25 °C. Error bars are not shown but the relative uncertainties are the same as in $\mu_{\text{W-W}}^{\text{E}}$, Figure 4 (a). (c) IL– H_2O interaction in terms of chemical potential, $\mu_{\text{IL-W}}^{\text{E}}$, in IL– H_2O at 25 °C. Error bars are not shown but the relative uncertainties are the same as in $\mu_{\text{W-W}}^{\text{E}}$, Figure 4a.

of $\text{I} < \text{OTF} < \text{BF4}$. This order is consistent with the properties of each IL toward H_2O in that I is a hydrophile,²⁵ OTF is amphiphilic,³ and BF4 is believed to be a hydrophobe. In Figure 4c, however, there could be an inflection point well below $x_{\text{IL}} < 0.1$, or the left of the small peak in the $\mu_{\text{IL-W}}^{\text{E}}$ vs x_{IL} curves

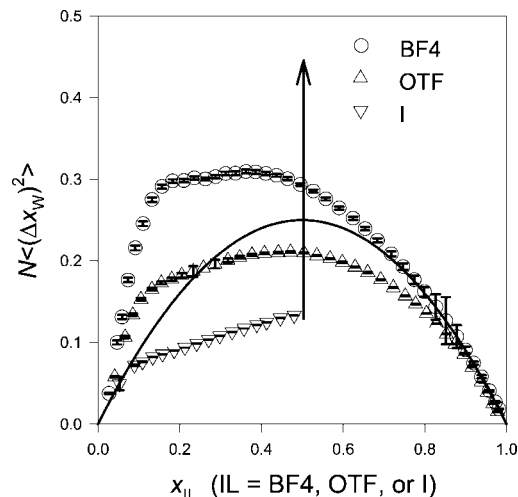


Figure 5. Concentration fluctuations, $N\langle(\Delta x_{\text{W}})^2\rangle$, in IL– H_2O at 25 °C. IL = BF4, OTF, or I. The solid line is for the ideal binary mixture. The vertical arrow indicates the divergence of $N\langle(\Delta x_{\text{W}})^2\rangle$ to infinity due to the first order phase separation. See text.

for BF4 and OTF. This sort of anomalous behavior is obscured in chemical potential level due to entropy–enthalpy compensation prevalent in aqueous solutions.^{28,29} More detailed discussion regarding the changes in mixing scheme ought to wait for the enthalpy and the entropy data.

Figure 5 shows the concentration fluctuation, $N\langle(\Delta x_{\text{W}})^2\rangle$, calculated by using the $\mu_{\text{W}}^{\text{E}}$ data, which have a smaller uncertainty than $\mu_{\text{IL}}^{\text{E}}$. Its definition is given by

$$N\langle(\Delta x_{\text{W}})^2\rangle = RT(1 - x_{\text{W}})/(\partial\mu_{\text{W}}/\partial x_{\text{W}}) \quad (8)$$

This quantity could also be determined by the scattering experiment. Indeed, a recent small angle neutron scattering study indicated that $N\langle(\Delta x_{\text{W}})^2\rangle$ showed a sharp peak at $x_{\text{IL}} \approx 0.08$ for $[\text{C}_4\text{mim}]\text{BF}_4-\text{H}_2\text{O}$ at 25 °C,³⁰ which is consistent with the data calculated by the right-hand side of eq 8 using our vapor pressure data.¹ The peak position coincided the upper critical solution point observed at 277 K.³¹ Thus at 25 °C, the system is in the super critical region with an enhanced concentration fluctuation. For the present aqueous solutions of $[\text{C}_2\text{mim}]$ based IL's, phase diagrams are not known. There is, however, a small shoulder beyond the error bar at about $x_{\text{IL}} < 0.1$ for BF4, as evident in Figure 5. Its significance is yet to be investigated. A similar shoulder may also be present for OTF and I systems also.

The arrow in Figure 5 for the I– H_2O system shows the divergence of $N\langle(\Delta x_{\text{W}})^2\rangle$ to infinity due to the phase separation at $x_{\text{IL}}(\text{IL}=\text{I}) = 0.503$, because in the two phase region $(\partial\mu_{\text{W}}/\partial x_{\text{W}})$ is identically zero. See eq 8. The observation in Figure 5 that the value of $N\langle(\Delta x_{\text{W}})^2\rangle$ for I– H_2O remains finite (and small) in the single phase region, $x_{\text{IL}} < 0.5$, indicates that this transition is of the first order in Ehrenfest's classification or the discontinuous kind in modern terminology,³² contrasting for example the cases for isobutiric acid– H_2O ³³ and acetonitrile– H_2O ^{34,35} systems near the respective critical point of liquid–liquid phase separation, where $(\partial\mu_{\text{W}}/\partial x_{\text{W}})$ becomes very small and hence $N\langle(\Delta x_{\text{W}})^2\rangle$ becomes very large even in the single phase domain. It is thus how small or large the slope of μ_{W} , $(\partial\mu_{\text{W}}/\partial x_{\text{W}})$, is that dictates divergence or nondivergence in $N\langle(\Delta x_{\text{W}})^2\rangle$ in a single phase region. Near the critical point that is classified as the second order or the continuous transition,³² the value of $(\partial\mu_{\text{W}}/\partial x_{\text{W}})$ is inevitably close to zero.

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Supporting Information Available: Table containing the vapor pressures and the excess chemical potentials, the data of W–W, IL–IL, and IL–W interactions in terms of chemical potential, and the concentration fluctuations are available free of charge via the Internet at <http://pubs.acs.org>.

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