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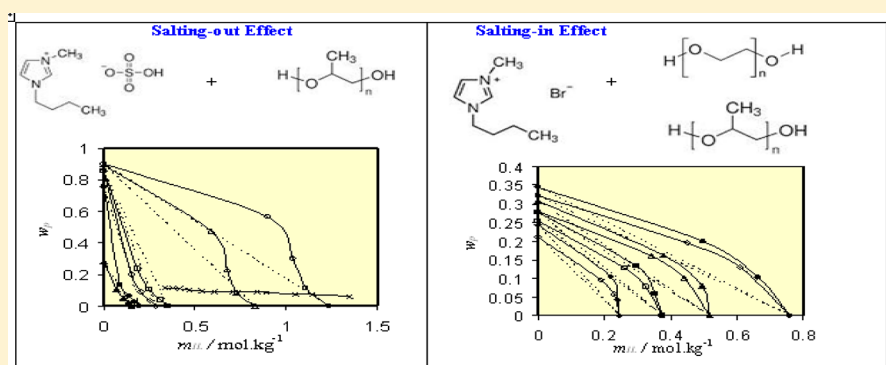
Isopiestic Investigations of the Interactions of Water-Soluble Polymers with Imidazolium-Based Ionic Liquids in Aqueous Solutions

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S *Supporting Information*

ABSTRACT: To provide insight into the salting effects produced by the addition of hydrophilic ionic liquids to aqueous solutions of water-soluble polymers and to obtain a relation between the vapor−liquid and liquid−liquid equilibrium behavior of ionic liquid−polymer aqueous−biphasic systems, the isopiestic equilibrium molalities of some ternary ionic liquid−polymer−water systems in both the one- and two-phase areas together with the liquid−liquid equilibrium phase diagrams for systems capable of inducing phase separation were determined at 298.15 K. The polymers are poly(ethylene glycol) 400 (PEG400), poly(ethylene glycol) 2000 (PEG2000), poly(ethylene glycol) 6000 (PEG6000), poly(ethylene glycol) 10 000 (PEG10 000), poly(propylene glycol) 400 (PPG400), and poly(propylene glycol) 725 (PPG725), and the investigated ionic liquids are 1-butyl-3-methylimidazolium bromide ($[C_4mim][Br]$) and 1-butyl-3-methylimidazolium hydrogen sulfate ($[C_4mim][HSO_4]$). It was found that aqueous solutions of $[C_4mim][HSO_4]$ form aqueous biphasic systems with PPG400 and PPG725 (salting-out effect); however, other investigated systems do not form aqueous biphasic systems (salting-in effect). A relationship was found between the salting-out and salting-in effects of ionic liquids on aqueous polymer solutions and the slopes of the constant water-activity lines for ternary ionic liquid−polymer aqueous solutions so that in the case of the salting-out effect the constant water-activity lines had a concave slope, but in the case of the salting-in effect the constant water-activity lines had a convex slope.

INTRODUCTION

Aqueous biphasic systems (ABS) are usually formed by mixing two structurally different polymers or one polymer and one salt in an aqueous solution above a certain critical concentration. Liquid−liquid extraction utilizing ABS has found this platform to be a powerful technique for purification, extraction, and enrichment both in industry and academia.[1,2] Ionic liquids (ILs) are a new type of ionic solvent that exists as a liquid below 373.15 K. Because ILs possess some green characteristics, such as negligible volatility, nonflammability under ambient conditions, a large liquid range, high thermal and chemical stability, strong solubility power, and a number of possible variations in cation and anion features that allow the fine-tuning of their properties, they have been gaining exposure for their potential uses as green solvents and possible replacements for traditional volatile organic compounds (VOCs) in a variety of applications.[3] Furthermore, in recent years it was found that a new class of IL-based ABS can be formed when a hydrophilic IL and a certain salt or a certain

water-soluble polymer are combined in an aqueous solution. In other words, in the case of polymer−salt ABS, both the polymer and salt can be replaced by a particular IL to form a new IL−polymer or IL−salt ABS. In fact, the thermodynamic properties of aqueous solutions of ILs depend on their structure and can be similar to those of either aqueous polymer solutions or aqueous salt solutions.[4] Unlike IL−salt ABS,[3,5] information about IL−polymer ABS is relatively scarce in the literature.[6−12] In a continuation of our previous work on the salting-out and salting-in of ILs[13] and water-soluble polymers[14] by electrolytes and in an attempt to obtain further evidence on the salting effect produced by the addition of ILs to aqueous solutions of different water-soluble polymers, we investigated a series of ternary systems containing water-soluble polymers and ILs that were or were not capable of inducing phase separation. To

cover a range of kosmotropic and chaotropic behaviors, polymers poly(ethylene glycol) 400 (PEG400), poly(ethylene glycol) 2000 (PEG2000), poly(ethylene glycol) 6000 (PEG6000), poly(ethylene glycol) 10 000 (PEG10 000), poly-(propylene glycol) 400 (PPG400), and poly(propylene glycol) 725 (PPG725) and ionic liquids 1-butyl-3-methylimidazolium bromide ($[C_4mim][Br]$) and 1-butyl-3-methylimidazolium hydrogen sulfate ($[C_4mim][HSO_4]$) were investigated. According to previous studies on IL—salt ABS, 1-butyl-3-methyl-imidazolium-based ($[C_4mim]^+$) ionic liquids are commonly used for extraction purposes because when they are combined with adequate anions the immiscibility of the resulting IL in water represents an additional advantageous property for dealing with the recovery of products from aqueous environments;[15] therefore, they are the most adequate ILs and have been comprehensively investigated as model ionic liquids for studying the salt effect in aqueous solutions. Because the polymer is salted-out by IL in IL—polymer ABS, a hydrophilic IL is required to study the salt effect. In this respect, $[C_4mim][Br]$ and $[C_4mim][HSO_4]$ are two good candidates with different hydrophilic properties. To investigate the relationship between the vapor—liquid and liquid—liquid equilibrium behavior of IL—polymer ABS, the isopiestic equilibrium molalities of binary polymer—IL—water and ternary polymer—IL—water systems in both the one- and two-phase areas together with liquid—liquid equilibrium phase diagrams of the polymer—IL ABS containing the above-mentioned water-soluble polymers and ILs were determined. These studies show for the first time that there is a relationship between the salting effect of ILs on aqueous polymer solutions and the slopes of the constant water-activity lines of the corresponding ternary polymer—IL aqueous solutions.

■ EXPERIMENTAL SECTION

Materials. PPGs were obtained from Fluka. PEGs, NaCl (>99.5% w/w), $[C_4mim][Br]$ (>99.0% w/w), and $[C_4mim]$-$[HSO_4]$ (>99.0% w/w) were obtained from Merck. PPGs and PEGs were used without further purification. NaCl was dried in an electric oven at 383.15 K for 24 h prior to use. ILs were dried under high vacuum at 333.15 K with a rotary evaporator for at least 4 h at 0.7 kPa. During the experiments, the moisture within the ILs was controlled by the Karl Fischer method and was taken into consideration in all of the calculations. Double-distilled deionized water was used for the preparation of the solutions.

Experimental Procedures. The solubility curves were established at 298.15 ± 0.05 K under atmospheric pressure through the cloud-point titration method.[16] A glass vessel with an external jacket in which water was circulated at a constant temperature using a thermostat was used to carry out the phase-equilibrium determinations. The liquid—liquid equilibrium phase diagram was determined by the repetitive dropwise addition of an aqueous IL solution of a known concentration to an aqueous polymer solution of a known concentration or vice versa until a cloudy solution (biphasic region) was detected, followed by the dropwise addition of water until a clear solution (monophasic region) was formed. The composition of the mixture was determined by its mass using an analytical balance with a precision of ±1 × 10⁻⁴ g.

The isopiestic apparatus used in this work to obtain the water activities of the different systems was similar to the one used by Ochs et al.,[17] whose details are similar to another one used previously.[14] This method is based on the phenomenon that different solutions with only one common solvent, when connected through the vapor space, approach equilibrium by transferring solvent mass through distillation. The equilibrium is established once the temperature and pressure are uniform throughout the system, provided that no concentration gradients exist in the liquid phase. At equilibrium, the chemical potentials of the solvent and the solvent activities in each of the solutions in the closed system are identical. Because the solvent activity is known for one or more standard solutions, it will be known for each solution within the isopiestic system. In all of the isopiestic measurements, NaCl solutions were used as an isopiestic standard. The apparatus consisted of a multileg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solution, one flask contained the pure polymer solution, one flask contained the pure IL solution, two or three flasks contained the polymer—IL—water solutions, and the central flask was used as a water reservoir. The apparatus was held in a constant-temperature bath for at least 5 days (depending on the concentration of the solutes) to reach equilibrium. The temperature was held at 298.15 ± 0.05 K. After equilibrium had been reached, the manifold assembly was removed from the bath, and each flask was weighed with an analytical balance to a precision of ±1 × 10⁻⁴ g. From the weight of each flask after equilibrium and the initial weights of IL and polymer, the mass fraction of each solution was calculated. The osmotic coefficients for the standard NaCl aqueous solutions have been calculated from a correlation given in the literature.[18]

■ RESULTS AND DISCUSSION

In this work, two sets of experiments were carried out to determine the relationship between the vapor—liquid equilibrium behavior and the capability of IL—polymer aqueous systems to undergo phase separation as well as to achieve further understanding of the salting effect produced by the addition of ILs to aqueous solutions of water-soluble polymers. To study the vapor—liquid equilibrium behavior, isopiestic equilibrium measurements at T = 298.15 K were carried out for the ternary $[C_4mim][Br]$ + PEG400 + H_2O, $[C_4mim][Br]$ + PEG2000 + H_2O, $[C_4mim][Br]$ + PEG6000 + H_2O, $[C_4mim]$-$[Br]$ + PPG400 + H_2O, $[C_4mim][HSO_4]$ + PEG400 + H_2O, $[C_4mim][HSO_4]$ + PEG10 000 + H_2O, $[C_4mim][HSO_4]$ + PPG400 + H_2O, and $[C_4mim][HSO_4]$ + PPG725 + H_2O solutions. For the systems that form ABS ($[C_4mim][HSO_4]$ + PPG400 + H_2O and $[C_4mim][HSO_4]$ + PPG725 + H_2O), the phase-diagram measurements at T = 298.15 K were also carried out to study their liquid—liquid equilibrium behavior. The measured vapor—liquid and liquid—liquid equilibrium data are presented in the Supporting Information of this Article.

For a certain IL/polymer aqueous solution that is in isopiestic equilibrium with a sodium chloride solution with molality m_{NaCl} and osmotic coefficient Φ_{NaCl}, the osmotic coefficient Φ was obtained according to

$$\Phi = \frac{2m_{NaCl}\Phi_{NaCl}}{2m_{IL} + m_p} \tag{1}$$

where m_{IL} and m_p are the molality of IL and polymer, respectively. From the experimental osmotic coefficients, it is possible to calculate the water activities, a_w, and vapor pressures, p, of the investigated solutions using the following equations

$$a_w = \exp[-M_w(2m_{IL} + m_p)\Phi] \qquad (2)$$

$$\ln a_w = \ln\left(\frac{p}{p_w^\circ}\right) + \frac{(B_w^\circ - V_w^\circ)(p - p_w^\circ)}{RT} \qquad (3)$$

where M_w is the molar mass of water, B_w° is the second virial coefficient of water vapor, V_w° is the molar volume of liquid water, and p_w° is the vapor pressure of pure water. In Figures 1–3, comparisons of the experimental osmotic coefficient,
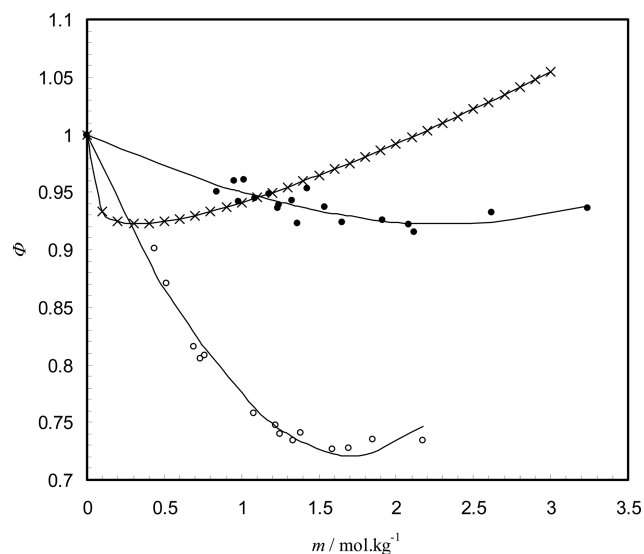

Figure 1. Osmotic coefficient Φ of the investigated binary aqueous solutions against molality, m, at T = 298.15 K. ○, $[C_4mim][Br]$ + H_2O; ●, $[C_4mim][HSO_4]$ + H_2O; ×, NaCl + H_2O; lines indicate Pitzer's model.

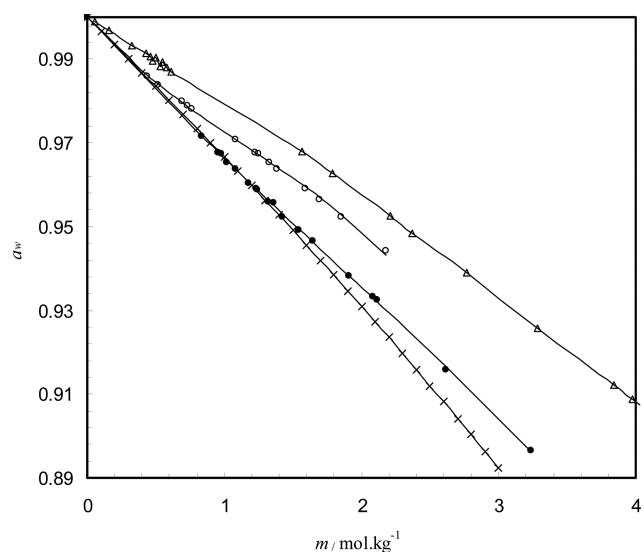**Figure 2.** Water activity, a_w, of the investigated binary aqueous solutions against molality, m, at T = 298.15 K. ○, $[C_4mim][Br]$ + H_2O; ●, $[C_4mim][HSO_4]$ + H_2O; ×, NaCl + H_2O; △, PEG200 + H_2O; lines indicate Pitzer's model.

water activity, and vapor-pressure depression data for the $[C_4mim][Br]$ + H_2O and $[C_4mim][HSO_4]$ + H_2O systems have been made at T = 298.15 K, respectively. The HSO_4^- anion can hydrogen bond with water molecules, and it hydrates
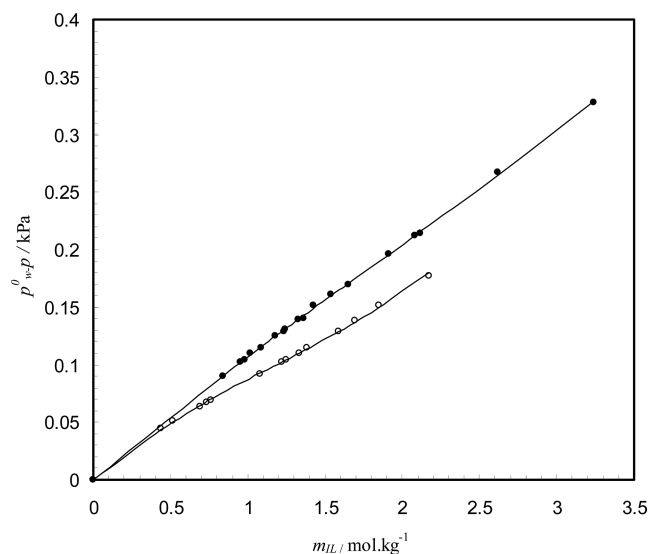

Figure 3. Vapor-pressure depression, $p_w^0 - p$, of the investigated binary aqueous solutions against the molality of IL, m_{IL}, at T = 298.15 K. ○, $[C_4mim][Br]$ + H_2O; ●, $[C_4mim][HSO_4]$ + H_2O; lines indicate Pitzer's model.

more water molecules than the Br^- anion. Therefore, we may expect the vapor-pressure depression for $[C_4mim][HSO_4]$ solutions will be greater than those for $[C_4mim][Br]$ solutions. Furthermore, protonation/deprotonotion equilibria associated with HSO_4^- lead to production of SO_4^{2-}, which strongly hydrates in aqueous solutions. The IL-molality dependence of the water activity or vapor-pressure depression follows the order $[C_4mim][HSO_4]$ > $[C_4mim][Br]$, which implies that the HSO_4^-–water interaction is stronger than the Br^-–water interaction. In Figure 2, the water activity data for the NaCl + H_2O[18] and PEG200 + H_2O[19] systems have also been given. As can be seen, at the same molality the values of the water activity of NaCl aqueous solutions are closer to those of $[C_4mim]$-$[HSO_4]$ aqueous solutions than to those of $[C_4mim][Br]$ aqueous solutions. However, the values of the water activity for the PEG200 + H_2O system are closer to those for the $[C_4mim][Br]$ + H_2O system. The behavior of the investigated ILs can be further compared if we consider the plots of the apparent molar volume, ϕ_V, as a function of IL molality. In Figure 4, the apparent molar volumes of ILs $[C_4mim][HSO_4]$ (determined in this work) and $[C_4mim][Br]$[20] in aqueous solutions have been compared at 298.15 K. As can be seen, similar to simple electrolytes,[21−24] the apparent molar volumes of $[C_4mim][HSO_4]$ in water increased by increasing the IL molality. At low salt concentrations, the small volume is attributed to the strong attractive interactions resulting from the hydration of ions. With increasing salt concentration, the ion−ion interaction increases, and the positive initial slope of ϕ_V against the salt concentration is attributed to these interactions. However, the values of ϕ_V of $[C_4mim][Br]$ in water decreased very slightly upon increasing the IL molality. This behavior is similar to that of aqueous polymer solutions.[25] Therefore, we can conclude that the properties of ILs $[C_4mim][HSO_4]$ and $[C_4mim][Br]$ are similar to those of simple electrolytes and water-soluble polymers, respectively, and in the case of the polymer−salt ABS, the polymer can be replaced by $[C_4mim][Br]$ to form a new IL−salt ABS,[13,20] and the salt can be replaced by $[C_4mim][HSO_4]$ to form a new IL−polymer ABS. Furthermore, the plots of water activity against
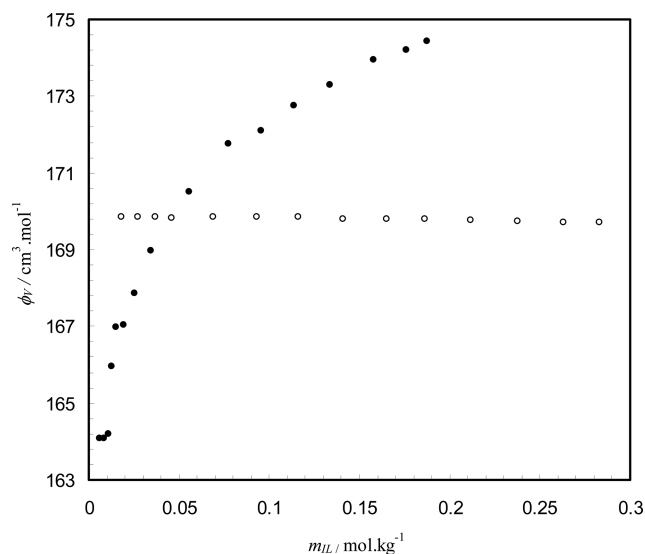
Figure 4. Apparent molar volume, ϕ_V, of the investigated ILs in aqueous solutions against the molality of IL, m_{IL}, at $T = 298.15$ K. $\bigcirc$, $[C_4mim][Br] + H_2O$; $\bullet$, $[C_4mim][HSO_4] + H_2O$.

Figure 5. Mole-fraction mean ionic activity coefficient, $\gamma_{\pm}^x$, ($\triangle$ and $\blacktriangle$) and water activity coefficient, γ_w, ($\bigcirc$ and $\bullet$) of the investigated binary aqueous solutions against the molality of IL, m_{IL}, at $T = 298.15$ K. $\bigcirc$ and $\triangle$, $[C_4mim][Br] + H_2O$; $\bullet$ and $\blacktriangle$, $[C_4mim][HSO_4] + H_2O$.

the molality of the ILs exhibit a change in the slope at a molality of ~1.5 mol·kg⁻¹, which may be due to the weak micellization of the ILs.

The water activity was used to obtain the solvent activity coefficient, γ_w, which is equal to $a_w \cdot x_w^{-1}$. From the experimental osmotic coefficient data and Pitzer's model,[26,27] the mean molal activity coefficients, $\gamma_{\pm}$, at molality, m', were calculated using the following relation

$$\ln \gamma_{\pm} = \Phi' - 1 + \int_0^{m'} \frac{\Phi - 1}{m} \, dm \tag{4}$$

where Φ' is the osmotic coefficient of the solution at molality m'. The following relation was used to obtain the mole-fraction mean ionic activity coefficient, $\gamma_{\pm}^{(x)}$, from the molal mean ionic activity coefficient, $\gamma_{\pm}$

$$\ln \gamma_{\pm}^{(x)} = \ln \gamma_{\pm} + \ln(1 + M_w \nu m) \tag{5}$$

Variations of γ_w and $\gamma_{\pm}^x$ with solute concentration are shown in Figure 5. For both systems, $\gamma_{\pm} < 1$ (i.e., negative deviations from ideal-solution behavior) and decreased along with an increase in the solute concentration. Furthermore, the observed trend for the calculated $\gamma_{\pm}$ of the investigated solutions is similar to those obtained for Φ and follows the order $[C_4mim][HSO_4] > [C_4mim][Br]$. The calculated water activity coefficients are very slightly smaller than unity and decrease slightly as the solute concentration increases and follows the order $[C_4mim][Br] > [C_4mim][HSO_4]$.

In this work, the isopiestic equilibrium molalities of different $[C_4mim][Br] + polymer + H_2O$ and $[C_4mim][HSO_4] + polymer + H_2O$ solutions were also determined at 298.15 K. For ternary aqueous electrolyte solutions under isopiestic equilibrium, the following empirical linear isopiestic relation (Zdanovskii–Stokes–Robinson rule) was proposed by Zdanovskii[28]

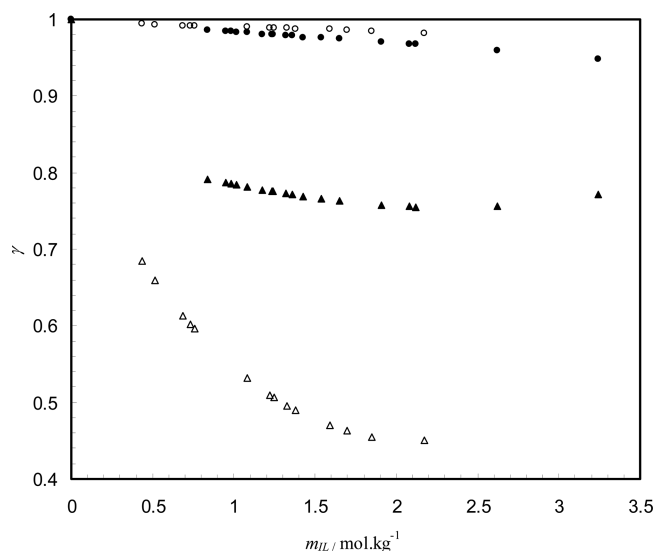$$\sum_i \frac{m_i}{m_i^0} = 1 \quad \left(a_w = \text{constant and } 0 \leq \frac{m_i}{m_i^0} \leq 1 \right) \tag{6}$$

where m_i is the molality of the solute, i, in the ternary solution, and m_i^0 is the molality of the solute, i, in the binary solution of equal a_w. Stokes and Robinson[29] derived this equation theoretically for isopiestic mixed-nonelectrolyte aqueous solutions from the semi-ideal hydration model. According to Zdanovskii's rule, binary aqueous solutions having equal water activity, when mixed in any proportion, will produce a ternary aqueous solution with the same water activity. In other words, many solutions with equal water activity exhibit no net-effective interaction when mixed; that is, changes in the solvation between the dissolved components upon mixing are apparently absent. Because the interactions between the solutes and the solvent occur and can be important in binary solutions but the interactions between the solutes in mixed solutions are not evident, the behavior is termed semi-ideal.[29,30] In fact, the thermodynamic behavior of the mixed solution (conforming to eq 6) is as simple as that of an ideal solution; that is, the constituent binary solutions are mixed ideally under isopiestic equilibrium.[29] Here we used the following form of the linear-isopiestic relation to test the obtained experimental constant water-activity lines of the investigated systems.

$$\frac{m_{IL}}{m_{IL}^0} + \frac{w_P}{w_P^0} = 1$$

$$\left(a_w = \text{constant, } 0 \leq \frac{m_{IL}}{m_{IL}^0} \leq 1 \text{ and } 0 \leq \frac{w_P}{w_P^0} \leq 1 \right) \tag{7}$$

The experimental constant water-activity lines of the different $[C_4mim][Br] + polymer + H_2O$ and $[C_4mim][HSO_4] + polymer + H_2O$ systems, along with the results of eq 7, are shown in Figures 6–10. As can be seen, for ternary aqueous mixtures of $[C_4mim][Br]$ in the presence of all of the investigated polymers, positive deviations from eq 7 were obtained, and the deviation for PEG400 is larger than that for PPG400. Although similar behavior was observed for all of the investigated ternary aqueous $[C_4mim][HSO_4] + PEG$ systems that were not capable of inducing phase separation, the positive
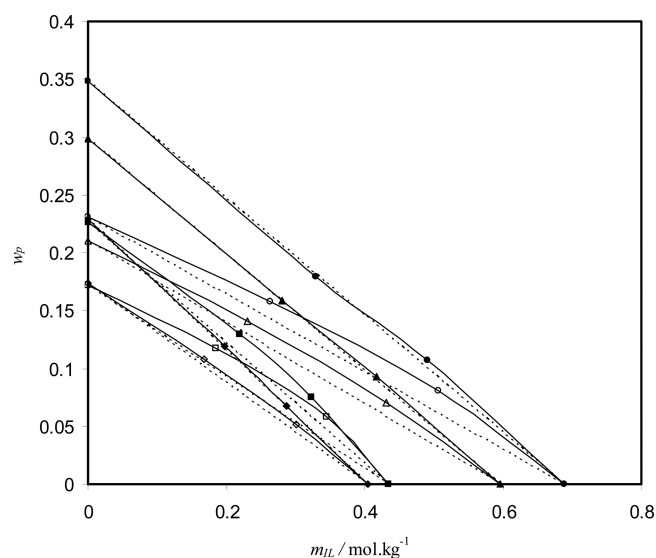
Figure 6. Plot of the mass fraction of the polymer, w_p, against the molality of $[C_4mim][Br]$, m_{IL}, for the constant water-activity curves of the PEG400 + $[C_4mim][Br]$ + H_2O (empty symbol) and PPG400 + $[C_4mim][Br]$ + H_2O (filled symbol) systems at T = 298.15 K. $\bigcirc$ and $\bullet$, a_w = 0.9800; $\triangle$ and $\blacktriangle$, a_w = 0.9829; $\square$ and $\blacksquare$, a_w = 0.9860; $\lozenge$ and $\blacklozenge$, a_w = 0.9885; and the dotted lines are calculated by eq 7.

Figure 7. Plot of the mass fraction of the polymer, w_p, against the molality of $[C_4mim][Br]$, m_{IL}, for the constant water-activity curves of the PEG2000 + $[C_4mim][Br]$ + H_2O (empty symbol) and PEG6000 + $[C_4mim][Br]$ + H_2O (filled symbol) systems at T = 298.15 K. $\bigcirc$ and $\bullet$, a_w = 0.9781; $\triangle$ and $\blacktriangle$, a_w = 0.9839; $\square$ and $\blacksquare$, a_w = 0.9883; $\lozenge$ and $\blacklozenge$, a_w = 0.9918; and the dotted lines are calculated by eq 7.

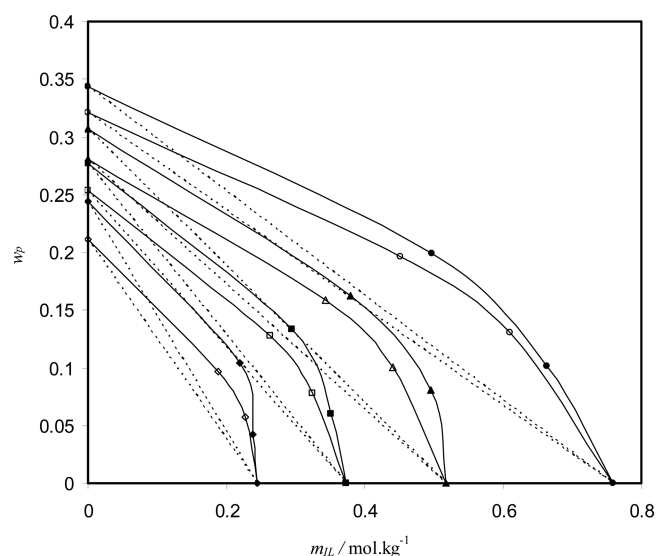**Figure 8.** Plot of the mass fraction of the polymer, w_p, against the molality of $[C_4mim][HSO_4]$, m_{IL}, for the constant water-activity curves of the PEG400 + $[C_4mim][HSO_4]$ + H_2O (empty symbol) and PPG400 + $[C_4mim][HSO_4]$ + H_2O (filled symbol) systems at T = 298.15 K. $\bigcirc$, a_w = 0.8968; $\triangle$, a_w = 0.9332; $\square$, a_w = 0.9557; $\lozenge$, a_w = 0.9717; $\bullet$, a_w = 0.7753; $\blacktriangle$, a_w = 0.8712; $\blacksquare$, a_w = 0.9326; $\blacklozenge$, a_w = 0.9461; $\times$, solubility curve; and the dotted lines are calculated by eq 7.
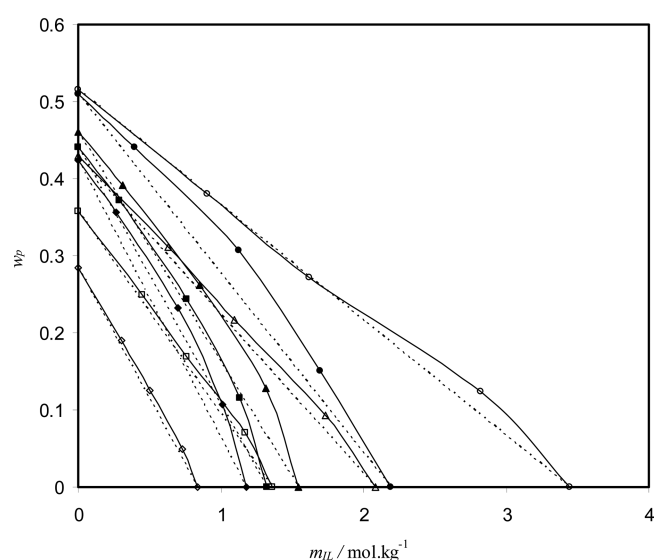
Figure 9. Plot of the mass fraction of the polymer, w_p, against the molality of $[C_4mim][HSO_4]$, m_{IL}, for the constant water-activity curves of the PEG400 + $[C_4mim][HSO_4]$ + H_2O (empty symbol) and PEG10000 + $[C_4mim][HSO_4]$ + H_2O (filled symbol) systems at T = 298.15 K. $\bigcirc$, a_w = 0.8968; $\triangle$, a_w = 0.9332; $\square$, a_w = 0.9557; $\lozenge$, a_w = 0.9717; $\bullet$, a_w = 0.9279; $\blacktriangle$, a_w = 0.9493; $\blacksquare$, a_w = 0.9560; $\blacklozenge$, a_w = 0.9605; and the dotted lines are calculated by eq 7.

deviation from eq 7 for the systems containing $[C_4mim][Br]$ is larger than that for systems containing $[C_4mim][HSO_4]$. However, in the case of the $[C_4mim][HSO_4]$ + PPG400 or PPG725 + H_2O systems, which form ABS, the constant water-activity lines in the one- and two-phase areas show the negative and positive deviation from eq 7, respectively. Furthermore, the negative deviation of the constant water-activity lines in the one-phase area derived from eq 7 for PPG725 is larger than that for PPG400.

These results show that there is a relationship between the salting-out and salting-in effects of ionic liquids on aqueous
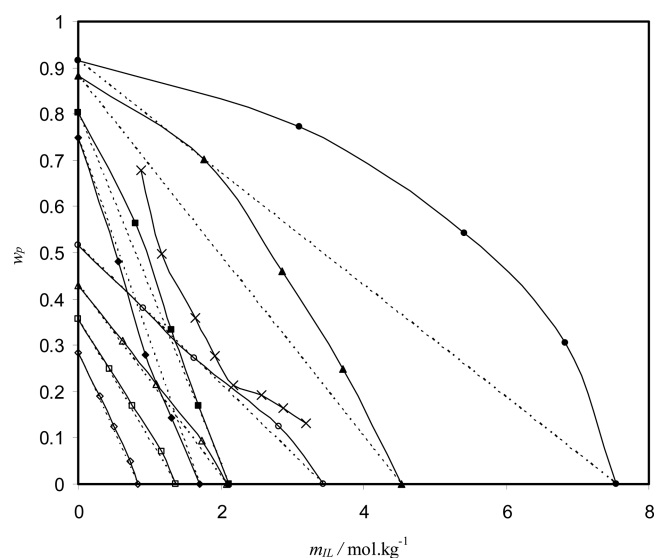
polymer solutions and the vapor–liquid equilibrium behavior of ternary aqueous IL–polymer systems, providing further support for our previous theories on the IL–salt[13] and polymer–salt[14] ABS. In fact, for the systems that conform to the linear isopiestic relation (eqs 6 and 7), the constituent binary solutions mix ideally under isopiestic equilibrium, and we can conclude that the solute–solvent interactions in the ternary solution are the same as those in the binary solutions. As can be seen from Figures 6–10, the positive and negative
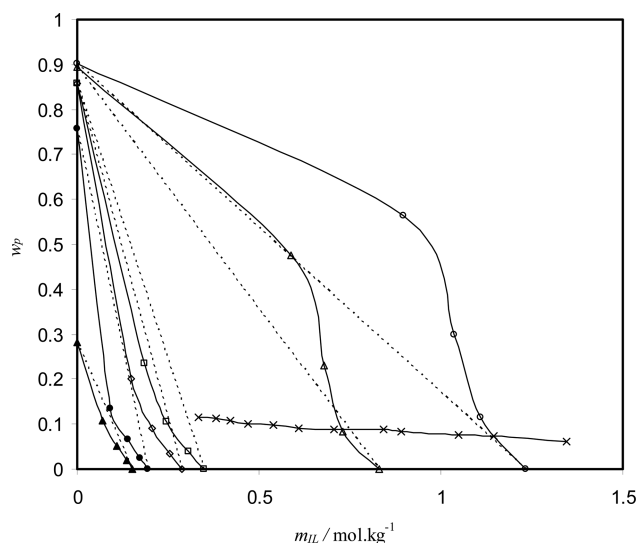
Figure 10. Plot of the mass fraction of PPG725, w_p, against the molality of $[C_4mim][HSO_4]$, m_{IL}, for the constant water-activity curves of the PPG725 + $[C_4mim][HSO_4]$ + H_2O system at T = 298.15 K. $\bigcirc$, a_w = 0.9588; $\triangle$, a_w = 0.9715; $\square$, a_w = 0.9873; $\lozenge$, a_w = 0.9894; $\bullet$, a_w = 0.9926; $\blacktriangle$, a_w = 0.9942; $\times$, solubility curve; and the dotted lines are calculated by eq 7.

deviations from the linear isopiestic relation (eqs 6 and 7) show that the concentrations of polymer and IL in a ternary solution in isopiestic equilibrium with certain binary polymer–water and IL–water solutions are larger and smaller, respectively, than those that we would expect for a semi-ideal solution (dotted lines).

For completely miscible polymer–IL solutions (salting-in effect) and as a consequence of preferential interactions between the salting-in inducing ions and polymer, the interaction of each solute with water becomes less favorable in the presence of the other solute; therefore, more free water molecules would be available with respect to a semi-ideal behavior in which the solute–solvent interactions in the ternary solution are same as those in the binary solution. Therefore, the concentrations of the polymer and IL in a ternary solution that is in isopiestic equilibrium with certain binary polymer–water and IL–water solutions are higher than those that we would expect for a semi-ideal solution (dotted lines), resulting in the expectation of salting-in effects for systems that show a positive deviation from eq 7. However, in the case of the $[C_4mim]$-$[HSO_4]$ + PPG400 and PPG725 + H_2O systems that form ABS (i.e., salting-out effect) and have unfavorable polymer–IL interactions, the interaction between solute 1 and water becomes more stable in the presence of solute two; therefore, in these ternary systems, fewer free water molecules would be available with respect to semi-ideal behavior, resulting in these systems showing a negative deviation from eq 7. Because the association between ions and a polymer is a highly unfavorable process, they exclude themselves from the vicinity of each other as a result of their preferential hydration. With increasing solute concentration, this exclusion will increase and ultimately the system could reach a state where, for entropic reasons, phase formation will become favorable. Similar to the polymer–IL interactions, the formation of aqueous two-phase systems involves the partial dehydration of the solutes; therefore, the interaction of each solute with water, which was stronger in the presence of the other solute, becomes weaker because of phase

separation, resulting in a positive deviation from eq 7 observed in the two-phase region. These results show that the solute–water interaction is an important property that controls the phase behavior of these systems; therefore, the water activity in these systems can provide useful information about the mechanisms of the salting effect produced by the addition of salting-out- or salting-in-inducing ILs to aqueous solutions of water-soluble polymers.

As mentioned above, the HSO_4^- anion can hydrogen bond with water molecules and is expected to be more effective than Br^- in the salting-out of polyethers because of the competition for water. Furthermore, the doubly charged SO_4^{2-} anion, produced from the protonation/deprotonation equilibria associated with HSO_4^- in aqueous media, has a marked salting-out effect on polymers. PPG contains a greater proportion of hydrocarbon in its molecule than PEG, and the side-chain methyl groups in PPG hinder hydrogen bonding between the water molecules and ether oxygen atoms; therefore, PPG can be more easily salted-out by a salting-out-inducing ion to form a polymer-based aqueous two-phase system than PEG. Therefore, the negative deviation of the constant water-activity lines from eq 7 for systems containing $[C_4mim][HSO_4]$ and PPG is larger than that for systems containing $[C_4mim][Br]$ and PEG. The hydrophobicity increases as the molecular weight of the PPG increases; therefore, PPG725 can be more easily salted-out by a salting-out-inducing ion to form a polymer-based aqueous two-phase system than PPG400, resulting in an increase in the negative deviation of the constant water-activity curves from eq 7 as the PPG molecular weight increases. Recently, Freire et al.[8] obtained a similar behavior for the different PEG–IL ABS. Furthermore, the above explanation correlates well with previously reported binary-phase diagrams produced between poly(ethyl glycidyl ether) and several imidazolium-based ILs.[31] Watanabe et al.[31] demonstrated that the solubility behavior is largely dependent on the anionic nature of the ionic liquid, so anions with a lower hydrogen-bond basicity are more miscible with the polymers investigated than anions with a higher ability for creating ion–water complexes. In addition, the obtained trend for the polymer molecular weight also agrees with the affinity/miscibility patterns observed in PEG–IL binary systems, which means that higher-molecular-weight PEG polymers are less soluble in ILs and are more readily separated from aqueous media.[8,32]

CONCLUSIONS

To obtain a detailed understanding of the molecular-level interactions in the salting effect of water-soluble polymers on the addition of ILs $[C_4mim][HSO_4]$ and $[C_4mim][Br]$, the isopiestic equilibrium molalities of aqueous solutions of PPG400, PPG725, PEG400, PEG2000, PEG6000, and PEG10 000 in the presence of the ILs at 298.15 K as well as liquid–liquid equilibrium phase diagrams for the ternary aqueous $[C_4mim][HSO_4]$ + PPG400 and $[C_4mim][HSO_4]$ + PPG725 systems that form ABS were determined. It was found that there is a relationship between the salting-effect of ionic liquids and the deviations of the constant water-activity lines from the linear-isopiestic relation. In addition, the phase behavior of polymer–IL ABS is largely controlled by the net result of the competition between the ability of the solutes to interact with water as well as the favorable or unfavorable interactions that occur between the polymer and IL. For polymer–IL water systems that are not capable of inducing

phase separation (the salting-in effect) because of the favorable polymer−IL interactions, the water molecules are allowed to relax to the bulk state; therefore, the water activity of these ternary systems is larger than those that we expect for a semi-ideal solution of the same concentration. The result is that these systems show positive deviations from the linear-isopiestic relation and the salting-in effects are expected. However, in the case of the ternary aqueous polymer−IL solutions that form ABS (salting-out effect), the interaction between solute one and water becomes more favorable in the presence of solute two; therefore, the water activities of these ternary solutions in the one-phase region are smaller than those we expect for a semi-ideal solution of the same concentration. These systems show a negative deviation from the linear-isopiestic relation; therefore, the salting-out of the polymer by salt occurs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of vapor−liquid and liquid−liquid equilibrium data for the investigated polymer−IL−water systems examined in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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7717

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