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Liquid−Liquid Equilibria of Aqueous Two-Phase Systems Containing 1-Butyl-3-methylimidazolium Bromide and Potassium Phosphate or Dipotassium Hydrogen Phosphate at 298.15 K

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Liquid−liquid equilibria (LLE) for the aqueous 1-butyl-3-methylimidazolium bromide, [C$_4$mim]Br, + potassium phosphate and [C$_4$mim]Br + dipotassium hydrogen phosphate systems have been determined experimentally at 298.15 K. The effect of the type of salt on the binodal and tie-lines has been studied on the basis of effective excluded volume values of the salt obtained from fitting the binodal data to the binodal model and Gibbs free energy of hydration of the constituent ions. Furthermore, the extended NRTL model has been used for the correlation of the obtained tie-line data. The six binary adjustable model parameters for this local composition model have been estimated either simultaneously from correlation of the experimental tie-line data or in the calculation; the model parameters between ionic liquid and water or between salt and water have been initially correlated with the vapor−liquid equilibrium (VLE) of the corresponding binary systems, and then those between ionic liquid and salt have been correlated with the tie-line data. The results show that good agreement was obtained with the experimental data.

Introduction

Liquid−liquid extraction has often been a favored choice of the process engineer for the development of separation processes.[1] The design of safe and environmentally benign separation processes has an increasingly important role in the development of clean manufacturing processes and in the remediation of sites contaminated by an older generation of manufacturing technologies. In this respect a number of different approaches have been identified, including the use of water as a solvent,[2] the use of supercritical fluids,[3] and the use of ionic liquids (IL). Liquid−liquid extraction utilizing aqueous two-phase systems (ATPSs) has already been used to separate and purify various biological products,[4−6] metal ions, dyes, drug molecules, and small organic species[7,8] from the complex mixtures in which they are produced. An ATPS usually composed of two or more polymers, a polymer and a salt,[4−6] or two surfactants (including quaternary ammonium surfactants and anionic surfactants)[9,10] is considered to be environmentally friendly because there is no use of traditional volatile organic solvents (VOCs) in the whole process. The applications of polymer or surfactant-based ATPSs have been well documented.[11−13] However, most phase-forming polymers and surfactants have high viscosity, form an opaque solution, and sometimes interfere with the analysis of analytes.

Recently, room temperature ionic liquids (RTILs) have been gaining exposure for their potential use as green solvents and possible replacements for VOCs for the variety of applications including organic synthesis,[14,15] biphasic catalysis, separation and extraction processes,[16] and dissolution of biomaterials,[17] due to their unique characteristics. Besides having many properties of conventional organic solvents, such as excellent solvation qualities, a variable viscosity range, and a wide temperature range, ionic liquids are nonvolatile and exhibit excellent chemical and thermal stabilities.[15,18] These features of RTILs offer numerous opportunities for the modification of existing extraction processes and for the development of new extraction processes; especially, because of the facilitated solvent recovery using technologies as simple as flash distillation or stripping due to their nonvolatile nature, the application of ionic liquids for extraction processes is promising. More recently, a new type of ATPSs consisting of IL and salts was reported for recycle, metathesis, and study of the distribution ratios of short-chain alcohols[19] and for biochemical or drug separation.[20,21] This type of IL-based ATPS can be formed when a hydrophilic IL, such as 1-butyl-3-methylimidazolium chloride, [C$_4$mim]Cl, is contacted with concentrated solutions of the water-structuring salts, forming an upper IL-rich phase and a lower salt-rich phase, both of which are aqueous.[19] Gutowski et al.[19] have determined a few tie-lines for the system [C$_4$mim]Cl + K$_3$PO$_4$ + water and presented them as a figure. 1-Butyl-3-methylimidazolium bromide, [C$_4$mim]Br, is another hydrophilic IL that may be used as the phase-forming IL, with the water-structuring salts, such as potassium phosphate or dipotassium hydrogen phosphate, in separation industries.

This work is devoted to the study of the phase behaviors of IL-based ATPSs including phase diagrams and the effect of salt in the [C$_4$mim]Br + potassium phosphate and [C$_4$mim]Br + dipotassium hydrogen phosphate aqueous two-phase systems at 298.15 K that have not been previously published. The obtained results are necessary for the design of extraction processes, understanding of general factors determining partition of solutes and particles in IL-based ATPSs, and development and testing of both thermodynamic and mass transfer models of aqueous two-phase systems. As the local composition nonrandom two liquid (NRTL) activity coefficient model is a comprehensive molecular thermodynamic model for systems with molecular and ionic species, molecules and ions of various size, and hydrophobic, hydrophilic, and amphiphilic species that can successfully be used for polymer systems,[22] aqueous

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electrolyte solutions,[23,24] and organic electrolyte systems.[24] In this work, the possibility of using the extended NRTL model[25] proposed to describe the liquid−liquid equilibria (LLE) for aqueous polymer−salt systems has been examined for the correlation of LLE data of the investigated IL−salt aqueous two-phase systems.

Experimental Section

Materials. [C_4mim]Br was obtained from Solvent Innovation Co.[26] (Köln, Germany) with a quoted purity of greater than 0.98 mass fraction and used without further purification. Water contents in the ionic liquid were determined by the Karl Fischer method to be less than 0.07 mass fraction. Potassium phosphate and dipotassium hydrogen phosphate with a minimum purity of 98 % by mass were supplied from Merck and used without further purification. Double-distilled deionized water was used for the preparation of solutions.

Apparatus and Procedure. The experimental apparatus employed is essentially similar to the one used previously.[27−29] The temperature was controlled to within ±0.05 °C. The binodal curves were determined by the cloud-point method.[4] A salt solution of known concentration was titrated with the ionic liquid solution or vice versa until the solution turned turbid, which indicated the formation of two liquid phases. In accordance with the amount of titrant added until turbidity was observed, the composition of the mixture for each point on the binodal curve was calculated by mass using an analytical balance (Shimadzu, 321-34553, Shimadzu Co., Tokyo, Japan) with a precision of $\pm 1 \cdot 10^{-7}$ kg. For the determination of the tie-lines, feed samples (about $2 \cdot 10^{-5}$ m^3) were prepared by mixing appropriate amounts of ionic liquid, salt, and water in the vessel. After sufficient mixing, the samples were placed in a water bath at the desired temperature and allowed to settle overnight to separate into two clear phases. Then, the concentration of salts in the top and bottom phases was determined by potassium analysis using flame photometry. The concentration of ionic liquid in both phases was also determined by refractive index measurements performed at 298.15 K using a refractometer (QUARTZ RS-232, Ceti, Belgium) with a precision of ±0.0001, and uncertainties in refractive index measurements are ±0.0002. For dilute aqueous solutions containing an ionic liquid and a salt, the relationship between the refractive index, n_D, and the mass fractions of ionic liquid, w_1, and salt, w_2, is given by

$$n_D = n_0 + a_1 w_1 + a_2 w_2 \tag{1}$$

where n_0 is the refractive index of pure water, which is set to 1.3325 at 298.15 K. This equation has been used for phase analysis of the polypropylene glycol + NaCl + H_2O system by Cheluget et al.[30]

With regard to the validity of the above procedure in the determination of tie-line compositions, the following explanations may be given: In the studied [C_4mim]Br + potassium phosphate + water and [C_4mim]Br + dipotassium hydrogen phosphate + water two-phase systems, as stated by Weingärtner,[31] the phenomenon of two-phase formation is probably a solvophobic one; therefore, in the investigated [C_4mim]Br + (K_3PO_4 or K_2HPO_4) + water two-phase systems, the hydrophilic IL, [C_4mim]Br, with a bulky organic cation is salted-out, as an ion pair, by the added or formed salt in the system containing a more cosmotropic anion (i.e., K_3PO_4 or K_2HPO_4, not KBr). In fact, these water structure making anions increase the dielectric constant of the aqueous phase, thus forcing the low dielectric [C_4mim]$^+$ cations to the upper phase with concurrent transfer of less cosmotropic bromide anions. To maintain the charge balance K^+ cations are also concentrated in the lower phase. This means that a salting-out effect leads to the formation of a biphasic system consisting of a [C_4mim]$^+$Br$^-$-rich upper phase and a $K^+PO_4^{3-}$- or $K^+HPO_4^{2-}$-rich lower phase. In this respect, this two-phase system resembles those formed in polymer−salt aqueous two-phase systems. A similar explanation has been given for [C_4mim]Cl as the phase forming IL in the [C_4mim]Cl+ K_3PO_4 + water system by Gutowski et al.[19] It must be noted that similar to what was observed by Gutowski et al.[19] for the aqueous [C_4mim]Cl+ K_3PO_4 two-phase system, due to the existence of equilibria of ions in two phases, the distribution ratios for the imidazolium and bromide ions are not exactly 1:1. However, to justify whether the amounts of salts and ionic liquid used to create the feed sample corresponded to the amounts in the top and bottom phases, we performed mass balance calculations and found that our procedure in the determination of the concentrations of salts in both phases using potassium analysis and those of ionic liquid by refractive index measurements is consistent with the mass balance calculations within ±1 %. Therefore, we concluded that the same method of calibration plots and evaluation of parameters given by Cheluget et al.[30] can also be used for the analysis of [C_4mim]Br + potassium phosphate + water and [C_4mim]Br + dipotassium hydrogen phosphate + water systems. Thus, the value of coefficient a_1 in eq 1 for both applied systems was obtained as 0.1624, and the value of coefficient a_2 was also obtained as 0.1834 and 0.1561 for the [C_4mim]Br + K_3PO_4 + H_2O and [C_4mim]Br + K_2HPO_4 + H_2O systems, respectively. However, it should be noted that this equation is valid only for dilute solutions ($w_1 \le 0.1$ and $w_2 \le 0.05$) for which linear calibration plots of the refractive index of ternary solutions with a fixed mass fraction of salt or ionic liquid against ionic liquid or salt are obtained. Therefore, before refractive index measurements, it was necessary to dilute the samples to the above mass fraction range.

Thermodynamic Framework

The excess Gibbs free energy, G^E, according to the extended NRTL model,[25] is expressed as the sum of three contributions

$$G^E = G^{E,\text{Comb}} + G^{E,\text{LR}} + G^{E,\text{SR}} \tag{2}$$

where $G^{E,\text{Comb}}$ is the combinatorial contribution, $G^{E,\text{LR}}$ is the long-range interaction contribution, and $G^{E,\text{SR}}$ is the short-range interaction contribution. The activity coefficient of component i (ionic liquid, ions, and water) can also be considered as the sum of three contributions:

$$\ln \gamma_i = \ln \gamma_i^{\text{Comb}} + \ln \gamma_i^{\text{LR}} + \ln \gamma_i^{\text{SR}} \tag{3}$$

The Flory−Huggins expression,[32] the Pitzer's extension of the Debye−Hückel function (PDH),[33] and the modified NRTL model[25] are used to calculate $G^{E,\text{Comb}}$, $G^{E,\text{LR}}$, and $G^{E,\text{SR}}$, respectively.

Combinatorial Contributions to the Excess Gibbs Free Energy. The Flory−Huggins equation together with the necessary procedure for obtaining $G^{E,\text{Comb}}$ has been given previously.[25,34] In the required relations for calculating the combinatorial contribution to the excess Gibbs free energy, $G^{E,\text{Comb}}$, and consequently to the activity coefficient of the component i, a value of $r = 1$ was used for the number of segments of water and the constituent ion salt. For the ionic liquid, the value of r is the ratio of the molar volume of ionic liquid to that of water. The molar volume of [C_4mim]Br may be estimated as $1.6909 \cdot 10^{-4}$ m^3·mol^{-1} from the infinite dilution apparent molal volume of [C$_4$mim]Br calculated from density data of aqueous solutions of [C$_4$mim]Br.[35] Recently, this method has been applied to the calculation of molar volumes of polyvinylpyrrolidone[36] and polyethylene glycols (PEGs).[37] Our result for the molar volume of [C$_4$mim]Br is in a good agreement with the value of $1.6844 \cdot 10^{-4}\ \mathrm{m^3 \cdot mol^{-1}}$ calculated using the density of pure [C$_4$mim]Br at 298.2 K reported by Kim et al.[38] The molar volume of liquid water at working temperature was also calculated using the density of pure water.[39]

Long-Range Interaction Contributions to the Excess Gibbs Free Energy. According to the extended NRTL model,[25] the PDH equation[33] normalized to the pure liquid electrolyte reference state was used to calculate the $G^{\mathrm{E,LR}}$. From appropriate differentiation of the PDH equation, one obtains the activity coefficient of a species i in the system as

$$\ln \gamma_i^{\mathrm{LR}} = -A_x \left[\frac{2Z_i^2}{\rho} \ln \left(\frac{1 + \rho I_x^{1/2}}{1 + \frac{\rho Z_i}{\sqrt{2}}} \right) + \frac{Z_i^2 I_x^{1/2} - 2I_x^{3/2}}{1 + \rho I_x^{1/2}} \right] \tag{4}$$

where

$$A_x = \frac{1}{3} \left(\frac{2\pi N_{\mathrm{A}}}{V_{\mathrm{s}}} \right)^{1/2} \left(\frac{e^2}{4\pi\epsilon D_{\mathrm{s}} KT} \right)^{3/2} \tag{5}$$

In the above relations, Z_k and ν_k are the charge number and stoichiometric number of ion k, respectively. ρ is the closest distance parameter. N_{A}, K, ϵ and e are Avogadro's number, the Boltzmann constant, the permittivity of vacuum, and the electronic charge, respectively. I_x is the ionic strength on a mole fraction basis, $I_x = 0.5\sum x_k Z_k^2$. The value of $\rho = 14.9$ has been frequently used for aqueous electrolyte solutions.[40] Therefore, this value was also used in this work. V_{s} and D_{s} are, respectively, the molar volume and dielectric constant of the mixed solvent (here, ionic liquid is assumed as the pseudo-solvent due to its tendency toward polymer-like behavior, as pointed out by some authors[15,41]). The necessary relations together with the procedure for obtaining V_{s} and D_{s} have been given previously.[34] As far as we know, there is no report on the dielectric constant of pure [C$_4$mim]Br in the literature, required for the calculation of D_{s}. In fact, the static dielectric constant of an ionic liquid is not measurable by conventional methods because the samples are largely short-circuited by their intrinsic electrical conductance. However, recently, many research groups have used a variety of alternative experimental polarity probes[42−44] to determine the dielectric constant, as this quantity is a key parameter for modeling solvent behavior and many approaches rely on dielectric continuum models for the solvent. However, polarity is not rigorously defined, and polarity scales depend on the experimental method used. Hence, reported polarities of ionic liquids differ substantially. More recently, the static dielectric constants of some widely used ionic liquids comprising imidazolium, pyridinium, pyrrolidinium, and alkylammonium cations were determined experimentally by microwave dielectric spectroscopy by Weingärtner.[45] He reported that the obtained results depend strongly on the nature of the anion and classified most ionic liquids as moderately polar solvents with dielectric constants of the order of $D_1 = 10$ to 12.[45] In this work, we found that the model parameters of the extended NRTL model are not considerably sensitive to the order of chosen D, as assuming different D values in the range of 10 to 40 produces very similar model parameters. Hence, in modeling the LLE data the dielectric constant of [C$_4$mim]Br was assumed to be $D = 11$. The dielectric constant of $D_3 = 78.33$ at 25 °C was also used for water.[46]

Table 1. Binodal Data for [C$_4$mim]Br (1) + Salt (2) + H$_2$O (3) Systems at 298.15 K

salt: K$_2$HPO$_4$				salt: K$_3$PO$_4$			
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
61.26	0.92	10.42	22.98	50.40	1.84	12.99	18.43
53.86	1.53	9.38	23.96	46.93	2.38	11.17	19.77
48.60	2.23	8.52	24.86	44.33	3.09	9.49	21.11
38.46	5.10	7.76	25.68	41.08	4.00	9.46	21.14
35.59	6.37	7.06	26.46	39.37	4.53	8.35	22.14
32.54	7.67			34.41	6.37	7.87	22.48
29.20	9.47			33.50	6.77	7.33	23.12
25.79	11.47			29.84	8.50	6.83	23.60
22.59	13.49			25.44	10.72	6.69	23.65
19.40	15.81			23.63	11.81	6.14	24.39
17.97	16.87			21.41	13.02	5.63	24.89
16.12	18.26			19.35	14.34	4.89	25.81
14.52	19.52			17.31	15.55	4.10	26.87
12.70	20.96			16.36	16.24	3.12	28.12
11.29	22.17			14.23	17.59	1.46	31.93

Short-Range Interaction Contributions to the Excess Gibbs Free Energy. The NRTL model extended by Zafarani-Moattar and Sadeghi[25] for aqueous polymer−salt systems can also be used for the correlation of experimental tie-line data for the studied systems. For an aqueous ionic liquid−salt system, the extended NRTL equation[25] for $G^{\mathrm{E,SR}}$ can be written as

$$\begin{aligned} \frac{G_{\mathrm{NRTL}}^{\mathrm{E,SR}}}{RT} = {} & n_{\mathrm{w}} \left[\frac{X_{\mathrm{il}} G_{\mathrm{sw}} \tau_{\mathrm{sw}} + (X_{\mathrm{c}} + X_{\mathrm{a}}) G_{\mathrm{ca,w}} \tau_{\mathrm{ca,w}}}{X_{\mathrm{w}} + X_{\mathrm{il}} G_{\mathrm{sw}} + (X_{\mathrm{c}} + X_{\mathrm{a}}) G_{\mathrm{ca,w}}} \right] + \\ & r n_{\mathrm{il}} \left[\frac{X_{\mathrm{w}} G_{\mathrm{ws}} \tau_{\mathrm{ws}} + (X_{\mathrm{c}} + X_{\mathrm{a}}) G_{\mathrm{ca,s}} \tau_{\mathrm{ca,s}}}{X_{\mathrm{w}} G_{\mathrm{ws}} + X_{\mathrm{il}} + (X_{\mathrm{c}} + X_{\mathrm{a}}) G_{\mathrm{ca,s}}} \right] + \\ & n_{\mathrm{c}} Z_{\mathrm{c}} \left[\frac{X_{\mathrm{w}} G_{\mathrm{w,ca}} \tau_{\mathrm{w,ca}} + X_{\mathrm{il}} G_{\mathrm{s,ca}} \tau_{\mathrm{s,ca}}}{X_{\mathrm{w}} G_{\mathrm{w,ca}} + X_{\mathrm{il}} G_{\mathrm{s,ca}} + X_{\mathrm{a}}} \right] + \\ & n_{\mathrm{a}} Z_{\mathrm{a}} \left[\frac{X_{\mathrm{w}} G_{\mathrm{w,ca}} \tau_{\mathrm{w,ca}} + X_{\mathrm{il}} G_{\mathrm{s,ca}} \tau_{\mathrm{s,ca}}}{X_{\mathrm{w}} G_{\mathrm{w,ca}} + X_{\mathrm{il}} G_{\mathrm{s,ca}} + X_{\mathrm{c}}} \right] \end{aligned} \tag{6}$$

The relation for the activity coefficient of a species i in the system can be obtained from appropriate differentiation of this equation. In the above relations the subscripts w, s, il, c, a, and ca stand for water, segment of ionic liquid, ionic liquid, cation, anion, and salt, respectively; n is the number of moles; and X is the effective local mole fraction and is given by

$$X_i = \phi_i K_i \quad (K_i = Z_i \text{ for ions and } K_i = \text{unity for ionic liquid and solvent}) \tag{7}$$

where ϕ_i is the segment fraction.[25] G and τ are energy parameters and are given by

$$\begin{gathered} G_{\mathrm{m'm}} = \exp(-\alpha \tau_{\mathrm{m'm}}) \\ \tau_{\mathrm{m'm}} = \frac{g_{\mathrm{m'm}} - g_{\mathrm{mm}}}{RT} \quad \tau_{\mathrm{j,ca}} = \tau_{\mathrm{jc,ac}} = \tau_{\mathrm{ja,ca}} \quad \tau_{\mathrm{ca,j}} = \tau_{\mathrm{cj}} = \tau_{\mathrm{aj}} \end{gathered} \tag{8}$$

Here, α is the nonrandomness factor and g is the energy of interaction. In the above relations the species m and m' can be solvent molecules, salt, or segments and the species j can be ionic liquid or solvent molecule.

Results and Discussion

Binodal Data. For aqueous [C$_4$mim]Br + potassium phosphate and [C$_4$mim]Br + dipotassium hydrogen phosphate

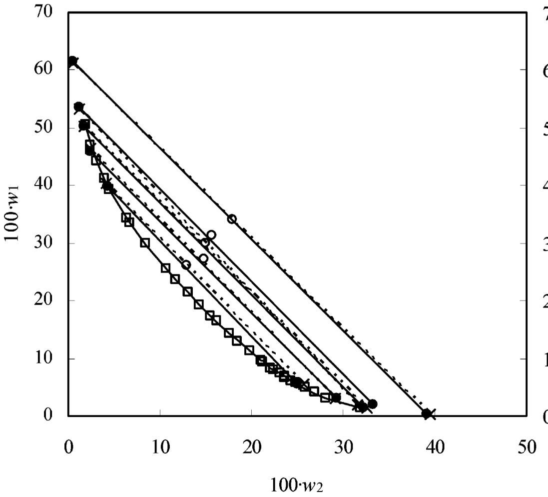

Figure 1. Phase diagram of the [C$_4$mim]Br (1) + K_3PO_4 (2) + H_2O (3) two-phase system at 298.15 K: □, experimental binodal; —, calculated binodal using eq 9; ○, total composition of tie-lines; —●—, experimental tie-lines; ···×···, calculated tie-lines with the extended NRTL model.

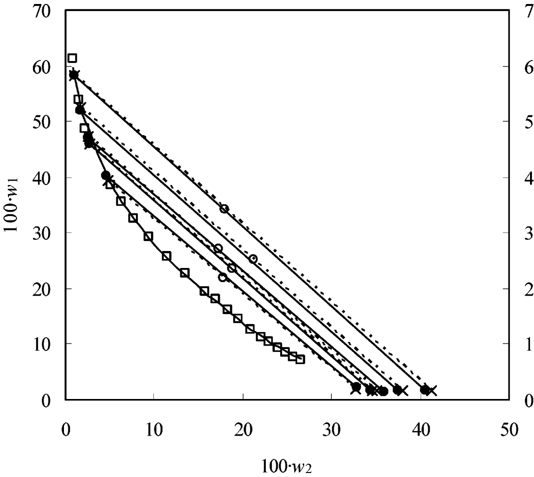

Figure 2. Phase diagram of the [C$_4$mim]Br (1) + K_2HPO_4 (2) + H_2O (3) two-phase system at 298.15 K: □, experimental binodal; —, calculated binodal using eq 9; ○, total composition of tie-lines; —●—, experimental tie-lines; ···×···, calculated tie-lines with the extended NRTL model.

systems the binodal data at 298.15 K are shown in Table 1 and were fitted by least-squares regression method to the following empirical nonlinear expression developed by Merchuk[47]

$$w_1 = a\,\exp(bw_2^{0.5} - cw_2^3) \qquad (9)$$

where w_1 and w_2 are the mass fractions of ionic liquid and salt, respectively. Recently, the above equation has been successfully used for the correlation of binodal data of some aqueous PEG−salt systems.[29,48] Using eq 9, the coefficients a, b, and c obtained from the correlation of experimental binodal data along with the corresponding standard deviations are given in Table 2. The binodals reproduced from eq 9 are also shown in Figures 1 and 2. On the basis of obtained standard deviations, we conclude that eq 9 can be satisfactorily used to correlate the binodal curves of the investigated systems.

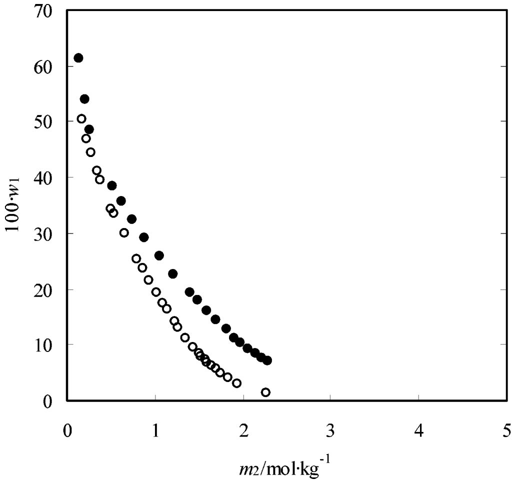

Figure 3. Effect of the type of salt on the binodal curves for the [C$_4$mim]Br (1) + salt (2) + H_2O (3) two-phase systems at 298.15 K: ○, K_3PO_4 ($V^*_{213} = 5.24 \cdot 10^{-3}$ kg·mol^{-1}); ●, K_2HPO_4 ($V^*_{213} = 3.60 \cdot 10^{-3}$ kg·mol^{-1}).

Table 2. Values of Parameters of Equation 9 for [C$_4$mim]Br (1) + Salt (2) + H_2O (3) at 298.15 K

system	a	b	$10^{-4}c$	10^2·sd[a]
[C$_4$mim]Br + K_3PO_4 + H_2O	76.34	−0.3087	0.6997	0.11
[C$_4$mim]Br + K_2HPO_4 + H_2O	81.44	−0.3248	0.4034	0.55

[a] sd = $(\sum_{i=1}^{N} (w_1^{\text{calcd}} - w_1^{\text{exptl}})^2/N)^{0.5}$, where N is the number of binodal data.

Table 3. Scaled Effective Excluded Volume of Salts for the [C$_4$mim]Br (1) + Salt (2) +H_2O (3) Systems at 298.15 K

salt	$10^3V^*_{213}$/(kg·mol^{-1})	f	10^2·sd
K_2HPO_4	3.60	0.39	2.79
K_3PO_4	5.24	0.27	1.02

The binodal model developed by Guan et al.[49] for aqueous polymer−polymer systems can also be used for the correlation of experimental binodal data for the studied systems. This model is based on the statistical geometry methods from which effective excluded volume (EEV) can be determined. The binodal equation for the aqueous ionic liquid−salt systems can be written as

$$\ln\left(V^*_{213}\frac{w_2}{M_2} + f_{213}\right) + V^*_{213}\frac{w_1}{M_1} = 0 \qquad (10)$$

where V^*_{213}, f_{213}, M_1, and M_2 are the scaled effective excluded volume (EEV) of salt, the volume fraction of unfilled effective available volume after tight packing of salt molecules into the network of ionic liquid molecules in ionic liquid aqueous solutions, which includes the influence of the size of the water molecules, and molar mass of ionic liquid and salt, respectively. For the investigated systems, the V^*_{213} and f_{213} values obtained from the correlation of the experimental binodal data along with the corresponding correlation coefficients and standard deviations are given in Table 3. On the basis of standard deviations presented in Tables 2 and 3, we conclude that in the correlation of the experimental binodal data, the binodal model, eq 10, with two parameters gives rather poor results. However, the rank order of the EEV values, (K_3PO_4, $5.24 \cdot 10^{-3}$ kg·mol^{-1} > K_2HPO_4, $3.60 \cdot 10^{-3}$ kg·mol^{-1}) indicates that the fitted parameter, V^*_{213}, should, in the investigated systems with a specific ionic liquid, be related to the salting-out strength of the salt, similar to aqueous polymer−salt systems.[29,48] To examine more closely the relation between the EEV values and the salting-out strength of the salts, the binodals of the investigated systems are plotted in Figure 3 where the concentration of ionic liquid is expressed in weight percentage, whereas those of the salts are given in molality. This is because the unit of EEV values of the salts should be in kg·mol^{-1}. As shown in Figure 3, the increase of

Table 4. Experimental Phase Equilibria for [C_4mim]Br (1) + Salt (2) + H_2O (3) at 298.15 K

total composition		top phase		bottom phase	
100 w_1	100 w_2	100 w_1	100 w_2	100 w_1	100 w_2
		Salt: K_3PO_4			
34.00	17.91	61.47	0.60	0.27	39.19
31.28	15.63	53.50	1.22	1.83	33.33
29.83	14.97	50.35	1.73	1.46	32.26
27.08	14.83	45.91	2.48	3.06	29.24
26.08	13.01	39.90	4.23	5.51	24.96
		Salt: K_2HPO_4			
34.09	18.01	58.20	1.02	1.69	40.65
25.08	21.29	51.98	1.72	1.68	37.49
27.03	17.38	46.95	2.58	1.44	36.03
23.64	18.90	45.96	2.70	1.69	34.34
21.85	17.86	40.30	4.64	2.11	32.82

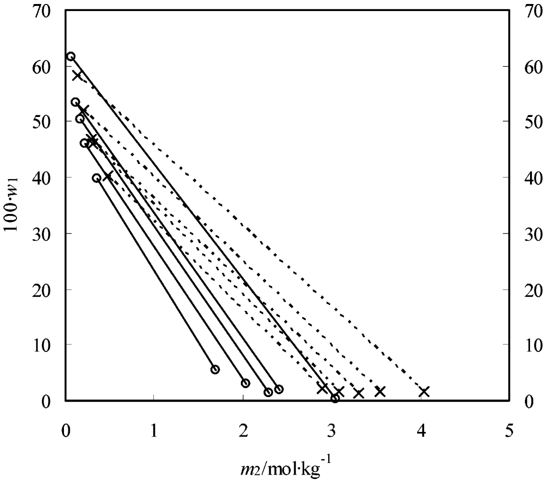

Figure 4. Effect of the type of salt on the tie-lines for the [C_4mim]Br (1) + salt (2) + H_2O (3) two-phase systems at 298.15 K: −○−, K_3PO_4; ···×···, K_2HPO_4.

the EEV value is reflected in the phase diagram by a shift in the position of the binodal curve to the left, corresponding to a decrease in the area representing the single-phase mixture; thus, a decrease in the concentration of the salt required to form a two-phase system indicates the higher salting-out strength of the salt.

Similar to aqueous polymer−salt two-phase systems, the salting-out ability of salts can also be related to Gibbs free energy of hydration of the constituent ions (ΔG_{hyd}).[29,50] The studied salts shared a common cation (K^+) but contained different anions of increasing charge; the anion with higher charge (with the same size[51]) is a better salting-out agent because the higher charge anion hydrates more water than the lower charge anion. This trend has also been observed for aqueous PEG−salt systems with the same phosphates.[52] Thus, it is easy to see that the anion with a higher salting-out ability has a more negative ΔG_{hyd} value

$$PO_4^{3-}, -2835\ \text{kJ·mol}^{-1} > HPO_4^{2-}, -1125\ \text{kJ·mol}^{-1}$$

where the ΔG_{hyd} values were calculated using the model proposed by Marcus.[51,53]

Tie-Lines. For aqueous [C_4mim]Br + potassium phosphate and [C_4mim]Br + dipotassium hydrogen phosphate systems the tie-line compositions at 298.15 K are given in Table 4 and presented in Figures 1 and 2, respectively. For the correlation of liquid−liquid equilibrium data of the investigated aqueous two-phase systems, the extended NRTL model[25] was used. Recently, the extended NRTL model has been used satisfactorily to correlate the liquid−liquid equilibrium data of some polymer−salt aqueous two-phase systems.[25,29,34] As pointed out by some authors,[15,41] ILs tend to display polymer-like behavior. Hence, to see the performance of the extended NRTL model in representing the LLE data for the investigated IL-based ATPSs, the tie-lines were fitted to this model.

The model parameters were estimated by minimizing the following objective function by the simplex method

$$\text{OF} = \sum_p \sum_l \sum_j (w_{p,l,j}^{\text{calcd}} - w_{p,l,j}^{\text{exptl}})^2 \tag{11}$$

where $w_{p,l,j}$ is the weight fraction of the component j in the phase p for lth tie-line and the superscripts calcd and exptl refer to the calculated and experimental values, respectively. In this equation, the species j can be ionic liquid, salt, or solvent molecule. The liquid−liquid equilibrium data of Table 4 were correlated using the equilibrium condition

$$(x_j\gamma_j)^{\text{top}} = (x_j\gamma_j)^{\text{bot}} \tag{12}$$

where the superscripts top and bot represent the top and bottom phases, respectively. For the extended local composition NRTL model, the six binary adjustable model parameters estimated simultaneously from correlation of the experimental tie-line data are given along with the corresponding deviations in Table 5. In the case of extended NRTL model, as stated by Chen,[22] the nonrandomness factor, in the range of 0.2 to 0.3, has no significant impact on the behavior of the used segment-based NRTL model. In this work, it has been fixed at 0.25. On the basis of the obtained deviations, given in Table 5, we conclude that this model can be satisfactorily used in representing the LLE data for these studied IL-based ATPSs. To show the reliability of the used model, comparisons between the experimental and correlated tie-lines are also shown in Figures 1 and 2.

Furthermore, to give plausible physical significance to the model parameters, in the case of the extended NRTL model, first the model parameters between the segments of the IL and water (τ_{sw} and τ_{ws}) have been obtained from the correlation of water activity data for aqueous [C_4mim]Br binary systems at working temperature. The necessary activity data have been calculated from the vapor pressure data of aqueous solutions of [C_4mim]Br reported by Kim et al.[54] and those presented by Shekaari in his Ph.D thesis that will be the subject of a future publication. The model parameters, $\tau_{\text{ca,w}}$ and $\tau_{\text{w,ca}}$, between salt and water are also calculated from vapor−liquid equilibrium (VLE) data of the corresponding electrolyte solution by simultaneously fitting the experimental electrolyte activity coefficients and the osmotic coefficients of water. The experimental data of aqueous K_3PO_4, and K_2HPO_4 binary systems at 298.15 K are taken from Robinson and Stokes.[46] The obtained correlation errors for these binary systems are very similar to

Table 5. Values of Parameters of the Extended NRTL Model for the [C_4mim]Br (s) + Salt (ca) + H_2O (w) Systems at 298.15 K

system	τ_{sw}	τ_{ws}	$\tau_{\text{ca,w}}$	$\tau_{\text{w,ca}}$	$\tau_{\text{ca,s}}$	$\tau_{\text{s,ca}}$	10^2·Dev[a]
[C_4mim]Br + K_3PO_4 + H_2O	1.0426	−0.1144	−3.1304	6.6966	10.8984	3.7534	0.28
[C_4mim]Br + K_2HPO_4 + H_2O	0.7478	−0.6501	−3.8148	7.5450	2.2973	116.00	0.17

[a] Dev = (OF/6N), where OF and N are objective function (eq 11) and number of tie-lines, respectively.

Table 6. Values of Parameters of the Extended NRTL Model for the [C_4mim]Br (s) + Salt (ca) + H_2O (w) Systems Using the Binary VLE Data for Aqueous Ionic Liquid and Salt Systems at 298.15 K

	$\alpha_{sw} = 0.25$		$\alpha_{ca,w} = 0.2$					
system	τ_{sw}	τ_{ws}	$\tau_{ca,w}$	$\tau_{w,ca}$	$\alpha_{ca,s}$	$\tau_{ca,s}$	$\tau_{s,ca}$	$10^2 \cdot$Dev
[C_4mim]Br + K_3PO_4 + H_2O	−0.9223	1.9535	−4.0156	8.5677	−0.0377	18.4979	−32.4109	0.68
[C_4mim]Br + K_2HPO_4 + H_2O	−0.9223	1.9535	−3.9428	8.4291	−0.0358	19.8425	−30.2160	0.64

those reported for the electrolyte NRTL model of Chen and Evans.[23] We do not show the results here.

The value of the nonrandom parameter, α, was set to 0.25 and 0.2 for the aqueous binary IL and salt systems, respectively. The value of α ($\alpha_{ca,s} = \alpha_{s,ca}$) was treated as an adjustable parameter, because the standard value (0.2 to 0.3) gave erroneous results. Other authors who investigated LLE data with ionic liquids also used other values for α other than the standard value.[55−58] Using the equilibrium condition, eq 12, and the model parameters ($\tau_{s,w}$, $\tau_{w,s}$, $\tau_{ca,w}$, $\tau_{w,ca}$) obtained from the correlation of VLE data, the model parameters, $\tau_{s,ca}$ and $\tau_{ca,s}$, between the segments of IL and salt were estimated from the correlation of experimental tie-line data of IL−salt ATPSs. The results of LLE fitting along with those obtained from the VLE data of the corresponding binary systems and standard deviations are given in Table 6. On the basis of the obtained deviations, given in Table 6, we conclude that the experimental LLE data for the investigated IL−salt ATPSs were successfully correlated with the extended NRTL model by this procedure.

Additionally, the slopes of the tie-lines for the investigated systems are compared. As can be seen from Figure 4, the slopes of tie-lines increase with increasing charge on the anion. This is because the anions with a higher charge or more negative ΔG_{hyd} value hydrate more water than the lower charged anions, thus decreasing the amount of water available to hydrate [C_4mim]Br. In Figure 4, to examine the effect of the type of salt on the slope of tie-lines in the investigated systems based on the ΔG_{hyd}, the concentration of ionic liquid in each phase is expressed in weight percentage, whereas those of the salts are given in molality. This is because the unit of ΔG_{hyd} values of the anions is in kJ·mol^{-1}.

Conclusions

Liquid−liquid equilibrium data for the aqueous [C_4mim]Br + potassium phosphate and [C_4mim]Br + dipotassium hydrogen phosphate systems were obtained at 298.15 K. Using the binodal model, the effective excluded volumes were calculated for these two systems. It was shown that, similar to aqueous polymer−salt systems, the effective excluded volume values are related to the salting-out strength of the salt. The effectiveness of the studied salts to form aqueous two-phase systems with [C_4mim]Br was also discussed on the basis of Gibbs free energy of hydration of salt constituent ions. It was found that for the studied systems an increase in the charge of the anion (with the same size) causes the expansion of the two-phase area and an increase of slopes of tie-lines. This is because the anions with a higher charge or more negative ΔG_{hyd} value hydrate more water than the lower charge anions. Furthermore, the use of the extended NRTL model has been tested in representing the phase behavior of these two ATPSs. The six binary adjustable model parameters for this local composition model have been estimated simultaneously from correlation of the experimental tie-line data. Good agreement was obtained with the experimental data with this model. Finally, to give plausible physical significance to the model parameters, in the calculation, the model parameters between ionic liquid and water or between salt and water have been initially obtained from the correlation of the vapor−liquid equilibrium of the corresponding binary systems, and then those between ionic liquid and salt have been estimated from the fitting of the tie-line data. Good agreement was also obtained with the experimental data with this procedure.

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