JOURNAL OF CHEMICAL & ENGINEERING DATA

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Solubilities of MCl (M = Na, K) in Aqueous Systems Containing the Ionic Liquid [Bmim]Cl from (298.15 to 343.15) K

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ABSTRACT: Solubilities of potassium chloride (KCl) and sodium chloride (NaCl) in aqueous systems containing the ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) were determined by cloud-point measurements using the laser beam scattering method in a temperature range of (298.15 to 343.15) K at atmospheric pressure. The solubility data were correlated and calculated with the Pitzer model modified by Harvie and Weare. The interaction parameters of the mixed-electrolyte solution were obtained using experimental results. It was found that the addition of [Bmim]Cl leads to salting-out, triggering a marked decrease of salt solubility in the aqueous solutions. The results also show that [Bmim]Cl has different salting-out ratios on KCl and NaCl in the mass-fraction range of $w_{[\mathrm{Bmim}]\mathrm{Cl}} = (0.025 \text{ to } 0.20)$. It is also shown that the modified Pitzer model gives a satisfactory prediction for the solubilities of KCl and NaCl in aqueous systems containing ionic liquid [Bmim]Cl.

INTRODUCTION

Ionic liquids (ILs) are organic salts which are typically a liquid at ambient temperature resulting from the combination of organic cations and various anions.[1] In recent years, ionic liquids have been widely applied in various fields, such as chemical syntheses, biocatalytic transformations, designing electrochemical devices, and analytical and separation processes.[2−5] They have received increasing attention from both industrial and academic communities.[6,7]

The thermodynamic properties of pure ILs and their mixtures are important for both theoretical studies and industrial applications. The experimental observations available indicate that the addition of inorganic salts to IL aqueous solutions affects the phase behavior.[8−10] Dupont et al.[11] witnessed the appearance of two coexisting phases in the water + 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) system by adding potassium chloride (KCl) at room temperature. By using a water-soluble ionic liquid and inorganic salt, Gutowski et al.[12] demonstrated that it is possible to form aqueous biphasic systems (ABS), i.e., the coexistence of two immiscible aqueous phases, via 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and a concentrated potassium phosphate K_3PO_4(aq) solution. Trindade et al.[13] investigated the effects of the addition of three inorganic salts (NaCl, Na_2SO_4, and Na_3PO_4) on the liquid−liquid phase diagram of aqueous solutions containing [Bmim][BF_4]. They found that all three inorganic salts can trigger the salting-out effect leading to a significant increase in the liquid−liquid demixing temperatures of the systems. Najdanovic-Visak et al.[14] observed a large salting-out effect by the addition of potassium phosphate to aqueous solutions of water-miscible ionic liquids. From ^{1}H NMR spectroscopy observations and molecular simulations, Freire et al.[15] gave a possible explanation for the salting-out and salting-in regimes for systems containing ILs and inorganic salt ions.

Most reports above were focused on the water + ionic liquid mixture forming an aqueous biphasic system due to the addition of inorganic salts. The solubility of inorganic salts in the aqueous systems is also influenced by adding ILs. In this work, the addition of ILs to water + inorganic salt systems was investigated. The solubility of MCl (M = K, Na) in aqueous solutions of [Bmim]Cl was measured by the cloud-point method using the laser beam scattering method from (298.15 to 343.15) K at atmospheric pressure. The basis of this method is to determine the concentration-dependent refractive index of an aqueous mixture. The scattering intensity of the laser beam passing through the glass cell is measured. The intensity drops continuously as long as the MCl concentration continues to increase. Once saturation of the solution is achieved, the refractive index of the aqueous solution remains constant. After exceeding the saturation MCl concentration, a number of small droplets form, and the solution becomes cloudy, scattering the light beam. By measuring the intensity of scattered light with time, it can be assessed whether the system is at equilibrium. Under an IL mass fraction of 0.25, the solutions were homogeneous at all experimental temperatures. In this work, no aqueous biphasic phenomenon was observed despite the addition of inorganic salts. The modified form of the Pitzer equation suggested by Harvie and Weare[16,17] was chosen to evaluate the average activity coefficients and the osmotic coefficients of chlorine-based salts and to calculate the solubilities of MCl (M = K, Na) in [Bmim]Cl + H_2O.

EXPERIMENTAL SECTION

Chemical Materials. KCl and NaCl (AR reagents from Shanghai Lingfeng chemical reagent factory) with a mass fraction purity greater than 0.998 were dried in a vacuum oven at 373.5 K

Special Issue: John M. Prausnitz Festschrift

Received: October 29, 2010
Accepted: February 8, 2011
Published: February 28, 2011

for 6 h before use. 1-Butyl-3-methyl imidazolium chloride ([Bmim]Cl) with a purity of 0.99 was purchased from Li Hua Chemicals (Henan, China) and was kept at 353.15 K under vacuum for over 8 h before use to remove moisture. ^{1}H NMR spectra and Raman spectrum results of the product were consistent with the literature.[18] Doubly distilled deionized water with a specific conductivity of approximately 1.3 $\mu\mathrm{S}\cdot\mathrm{cm}^{-1}$ was used for the preparation of solutions.

Apparatus and Procedures. The cloud-point concentration and phase separation of (water + [Bmim]Cl + salt) ternary systems were studied by the laser beam scattering method in the temperature range from (298.15 to 343.15) K at atmospheric pressure. The experimental samples were kept inside a glass cell at a constant temperature that was controlled by flow through the water jacket. This flow came from a thermostatic bath adjusted by a thermostat to maintain the required temperature in an accuracy of ± 0.1 K measured by a mercury thermometer in the jacket. The laser beam with wavelength 670.8 nm was generated from a laser diode source. The solutions were prepared by mass using a Sartorius analytical balance (model A200S) with an uncertainty of 0.1 mg.

Approximately 80 g of [Bmim]Cl solution was placed in the glass cell, and MCl was slowly added into the cell with stirring. By monitoring the scattering intensity of the laser beam, the saturation status was judged by the appearance of the cloud point observed at least 4 h. Finally, the solubility of MCl in the mixed solvent was calculated. Each experimental run was repeated three times, and the uncertainty was estimated to be ± 0.0035 g/(100 g solvent). Our measured solubilities of MCl by the laser beam scattering method are in agreement with the analytical gravimetric method.[23,24] The maximum difference between the two methods is only at 0.005 $\mathrm{mol}\cdot\mathrm{kg}^{-1}$ solvent.

THERMODYNAMIC MODEL

Description of the Model. One of the reliable electrolyte solution theories to describe the solubilities of salts in a mixed electrolyte solution is the Pitzer model, which gives a set of expressions for the osmotic coefficients of water and mean activity coefficients of electrolytes.[19] Harvie and Weare modified the Pitzer model to successfully predict mineral solubilities in complex brine systems.[16,17]

The expression for the solubility product, K_{sp}, of an anhydrous inorganic salt in mixed electrolyte solutions is

$$\ln K_{\mathrm{sp}} = \nu_{\mathrm{M}} \ln(m_{\mathrm{M}}\gamma_{\mathrm{M}}) + \nu_{\mathrm{X}} \ln(m_{\mathrm{X}}\gamma_{\mathrm{X}}) \tag{1}$$

where m_{M} and m_{X} represent the saturated molalities; γ_{M} and γ_{X} represent the ionic activity coefficients; and ν_{M} and ν_{X} represent the stoichiometric number, for the cation and anion, respectively.

According to Harvie and Weare,[16,17] the osmotic coefficient of water in a mixed electrolyte solution containing two salts MX and NX of the 1−1 type with a common anion X (in this work, M = Na^+ or K^+, X = Cl^-, and N = $[\mathrm{Bmim}]^+$) is given by

$$\phi - 1 = F + \frac{m}{m_0}[(1-y)B_{\mathrm{MX}}^{\phi} + yB_{\mathrm{NX}}^{\phi} + y(1-y)(\theta_{\mathrm{MN}} + I\theta_{\mathrm{MN}})] + \left(\frac{m}{m_0}\right)^2 [(1-y)C_{\mathrm{MX}} + yC_{\mathrm{NX}} + y(1-y)\psi_{\mathrm{MNX}}] \tag{2}$$

,where m_0 = 1 $\mathrm{mol}\cdot\mathrm{kg}^{-1}$; the symbol m is the molality of the common ion; y is the mole fraction of NX in MCl + [Bmim]Cl aqueous solution; and I is the ionic strength (for 1:1 electrolytes, $I = m$). The binary mixing parameter, θ_{MN}, takes into account interactions between unlike ions of the same sign. Additionally, the ternary mixing parameter, ψ_{MNX}, takes into account interactions between two unlike ions of the same sign and a third ion with the opposite sign. The long-range electrostatic term F is defined as

$$F = f' + \sum_{i=\mathrm{N}}^{\mathrm{M}} m_i m_{\mathrm{X}} B_{i\mathrm{X}}' + m_{\mathrm{M}} m_{\mathrm{N}} \theta_{\mathrm{MN}} \tag{3}$$

here

$$f' = -A^{\Phi}[I^{1/2}/(1+bI^{1/2}) + 2\ln(1+bI^{1/2})/b] \tag{4}$$

where b is a constant with a value of 1.2 $\mathrm{kg}^{1/2}\{\cdot\mathrm{mol}^{-1/2}$, and A^{Φ} is the Debye−Hückel constant for the osmotic coefficient. The dependence of A^{Φ} on temperature T (K) is expressed by[20]

$$A^{\Phi} = 0.13422(4.1725332 - 0.1481291T^{0.5} + 1.5188505\cdot 10^{-5}T^2 - 1.8016317\cdot 10^{-8}T^3 + 9.3816144\cdot 10^{-10}T^{3.5}) \tag{5}$$

The ionic activity coefficient is given by the following expressions.

For the cation:

$$\ln \gamma_{\mathrm{M}} = Z_{\mathrm{M}}^2 F + m_{\mathrm{X}}(2B_{\mathrm{MX}} + ZC_{\mathrm{MX}}) + m_{\mathrm{N}}(2\theta_{\mathrm{MN}} + m_{\mathrm{X}}\psi_{\mathrm{MNX}}) + \sum_{i=\mathrm{N}}^{\mathrm{M}} |Z_i| m_i m_{\mathrm{X}} C_{i\mathrm{X}} \tag{6}$$

For the anion:

$$\ln \gamma_{\mathrm{X}} = Z_{\mathrm{X}}^2 F + \sum_{i=\mathrm{N}}^{\mathrm{M}} m_i(2B_{i\mathrm{X}} + ZC_{i\mathrm{X}} + m_{\mathrm{X}}C_{i\mathrm{X}}) + m_{\mathrm{M}} m_{\mathrm{N}} \psi_{\mathrm{MNX}} \tag{7}$$

where

$$C_{\mathrm{MX}} = C_{\mathrm{MX}}^{\Phi}/(2|Z_{\mathrm{M}}Z_{\mathrm{X}}|^{1/2}) \tag{8}$$

and

$$Z = |Z_{\mathrm{M}}|m_{\mathrm{M}} + |Z_{\mathrm{X}}|m_{\mathrm{X}} + |Z_{\mathrm{N}}|m_{\mathrm{N}} \tag{9}$$

In these equations, Z_i and m_i represent the charge number and molality of each ion, respectively.

The second virial coefficients B^{Φ}, B, and B' are

$$B^{\phi} = \beta^0 + \beta' \exp(-\alpha\sqrt{I}) \tag{10}$$

$$B = \beta^0 + 2\beta'[1 - (1 + \alpha\sqrt{I})\exp(-\alpha\sqrt{I})]/\alpha^2 I \tag{11}$$

$$B' = \beta^0 - 2\beta'[1 - (1 + \alpha\sqrt{I} + \alpha^2 I/2)\exp(-\alpha\sqrt{I})]/\alpha^2 I^2 \tag{12}$$

The parameter α has been fitted to osmotic coefficients from (273 to 498) K and has a value of 1.4 $\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$.[21] The parameters β^0, β^1, and C^{Φ} are the ion interaction parameters which are functions of temperature and pressure.

Parameter Estimation. The K_{sp} value of MCl (M = K, Na) can be obtained from the solubilities of salts in pure water as a function of temperature.[22−25] Since it is a thermodynamic constant, the value of K_{sp} of MCl (M = K, Na) in an aqueous solution of [Bmim]Cl is the same as in pure water at the same temperature. Thus, it is possible to calculate saturated molality of

Table 1. Dimensionless Parameters of the Extended Pitzer Model for [Bmim]Cl + H_2O Aqueous Solutions at Different Temperatures T = (298.15 to 343.15) K

T/K	β^0	β^1	C^Φ
298.15[a]	0.04733	−1.20989	−0.01159
308.15[a]	0.00362	−0.87037	0.00145
313.15[b]	0.00693	−0.78424	0.00144
318.15[a]	0.00307	−0.71597	0.00143
328.15[a]	−0.01446	−0.53625	0.00796
333.15[b]	−0.04120	−0.37852	0.01877
343.15[c]	−0.18863	0.180263	0.06689

[a] Indicates the values in this row come from Shekaari et al.'s work. [b] Indicates the values were re-estimated by the modified Pitzer model. [c] Indicates the values were calculated using eq 13.

Table 2. Comparison of Our Experimental Values (Exptl) and the Literature Values (Lit.) for the Solubilities $m/(\mathrm{mol\cdot kg^{-1}})$ of KCl and NaCl in Pure H_2O From T = (298.15 to 343.15) K at p = 0.1 MPa[a]

T/K	298.15	308.15	313.15	318.15	328.15	333.15	343.15
			$m_{KCl}/(\mathrm{mol\cdot kg^{-1}})$				
Exptl	4.795	5.162	5.383	5.564	5.940	6.148	6.510
Lit.	4.80		5.39			6.15	6.51
			$m_{NaCl}/(\mathrm{mol\cdot kg^{-1}})$				
Exptl	6.16	6.194	6.229	6.248	6.304	6.348	6.425
Lit.	6.16		6.23			6.35	6.43

[a] Note: All the available literature values come from refs 22 to 24.

Table 3. Experimental Values $m/(\mathrm{mol\cdot kg^{-1}})$ of KCl and NaCl in Mixed [Bmim]Cl (1)+ H_2O (2) Aqueous Solutions at the Range of Temperatures T = (298.15 to 343.15) K and Mass Fraction w_1= (0.05 to 0.25) at p = 0.1 MPa

T/K	w_1 = 0.05	w_1 = 0.10	w_1 = 0.15	w_1 = 0.20	w_1 = 0.25
		$m_{KCl}/(\mathrm{mol\cdot kg^{-1}})$			
298.15	4.195	3.590	3.103	2.719	2.323
308.15	4.532	3.872	3.430	2.935	2.521
313.15	4.659	3.994	3.564	3.037	2.642
318.15	4.812	4.164	3.658	3.130	2.711
328.15	5.034	4.396	3.886	3.349	2.879
333.15	5.129	4.518	4.007	3.473	2.974
343.15	5.431	4.718	4.302	3.792	3.322
		$m_{NaCl}/(\mathrm{mol\cdot kg^{-1}})$			
298.15	5.355	5.039	4.406	3.597	2.795
308.15	5.378	5.062	4.411	3.655	2.862
313.15	5.408	5.086	4.452	3.657	2.883
318.15	5.433	5.103	4.466	3.653	2.901
328.15	5.442	5.120	4.463	3.673	2.920
333.15	5.499	5.140	4.518	3.733	2.940
343.15	5.510	5.171	4.530	3.714	2.971

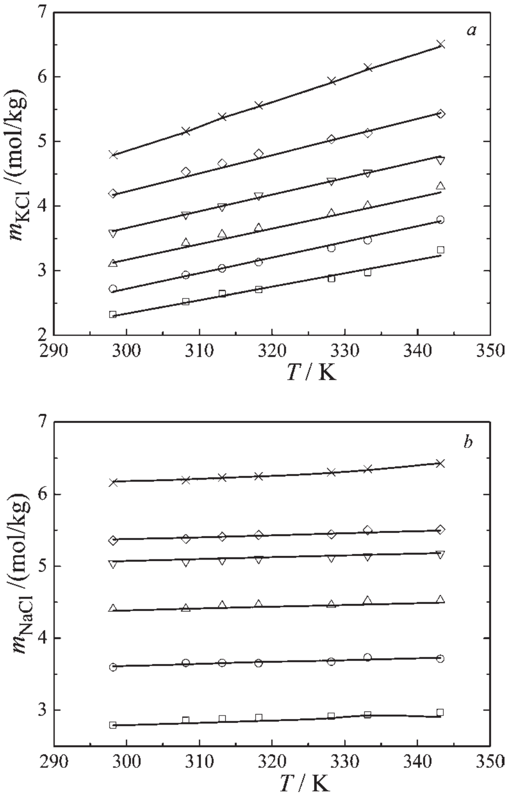

Figure 1. Comparison of experimental and calculated results of solubilities of KCl (a) and NaCl (b) in [Bmim]Cl (1) + H_2O (2) from w_1 = (0 to 0.25) as a function of temperature T. Solid lines are the calculated profile by the extended Pitzer model, and signs are the experimental data. Symbols: ×, w_1 = 0; ◇, w_1 = 0.05; ▽, w_1 = 0.10; △, w_1 = 0.15; ○, w_1 = 0.20; □, w_1 = 0.25.

MCl (M = K, Na) in the system containing water + [Bmim]Cl with the activity coefficients calculated by the modified Pitzer model containing parameters θ_{MN}, ψ_{MNX}, β^0, β^1, and C^Φ.[16,17] In the Pitzer model, these parameters, determined from a single electrolyte solution, can be further extended to a multicomponent electrolyte solution. For MCl (M = K, Na), these parameters β^0, β^1, and C^Φ are all functions of temperature at the given pressure, and the dependence on temperature (K) can be calculated as follows[25]

$$f(T) = d_1 + d_2(1/T - 1/T_R) + d_3\ln(T/T_R) + d_4(T - T_R) + d_5(T^2 - T_R{}^2) + d_6\ln(T - 260) \qquad (13)$$

where T_R = 298.15 K. The function $f(T)$ denotes $\beta^0(T)$, $\beta^1(T)$, and $C^\Phi(T)$ respectively, and the d_i terms are coefficients,[26,27] which can be used to estimate β^0, β^1, and C^Φ at different temperatures.

Shekaari et al.[28] have obtained β^0, β^1, and C^Φ for [Bmim]Cl from osmotic coefficients of water in the [Bmim]Cl + water system at (298.15 to 328.15) K, and these are listed in Table 1. Unfortunately, Shekaari et al. did not present experimental values at 313.15 K, 333.15 K, and 343.15 K. To obtain β^0, β^1, and C^Φ at the required temperature, the two sets of parameters at (313.15 and 333.15) K for [Bmim]Cl were re-estimated first using osmotic coefficients provided by González et al.[29] and the revised Pitzer model adopted here. Then, the coefficients d_i in eq 13 were regressed to the β^0, β^1, and C^Φ values obtained from (298.15 to 328.15) K. At 343.15 K, the parameters β^0, β^1, and C^Φ were calculated in terms of eq 13, and these results are also listed in Table 1. Only two parameters, θ_{MN} and ψ_{MNX}, are unknown in our adopted model, which have been fit to our experimental results.

■ RESULTS AND DISCUSSION

Experimental Results. The experimental values of solubility m (mol·kg^{-1}) of KCl and NaCl in the [Bmim]Cl + H_2O system at different temperatures T = (298.15 to 343.15) K are listed in Table 2 and Table 3, where the corresponding solubilities of salt in pure water (w_{IL} = 0) are also presented. The measured values in this work are close to those previously reported,[22−24] indicating their reliability. As evidenced in Figure 1, the solubility of KCl in [Bmim]Cl + H_2O increases steadily with temperature. Comparatively, the solubility of NaCl in [Bmim]Cl + H_2O increases significantly less with temperature. Figure 1 also shows that the solubility of MCl (M = K, Na) in [Bmim]Cl + H_2O decreases when the mass fraction of [Bmim]Cl is increased. These experimental results show that the presence of ILs can lower the solubility of MCl (M = K, Na) in an aqueous solution due to their salting-out effect.[30] For example, the solubility reduces by about 51 % for KCl and 55 % for NaCl for $w_{[\mathrm{Bmim}]\mathrm{Cl}}$ = 0.25 relative to pure water.

The salting-out ratio R can be estimated as follows

$$R = \frac{m_0 - m}{m_0} \qquad (14)$$

where m_0 is the solubility of inorganic salts in pure water. Figure 2 gives a comparison of salting-out ratio of [Bmim]Cl on KCl and NaCl at 298.15 K. From $w_{[\mathrm{Bmim}]\mathrm{Cl}}$ = (2.5 to 20)·10^{-2}, the salting-out ratio between KCl and NaCl deviates. This same phenomenon was also observed at the other experimental temperatures examined. From these observations, we can hypothesize that the crystallization area of KCl and NaCl in ternary system of KCl + NaCl + H_2O might be manipulated by the addition of an appropriate ionic liquid, allowing the separation of KCl and NaCl.

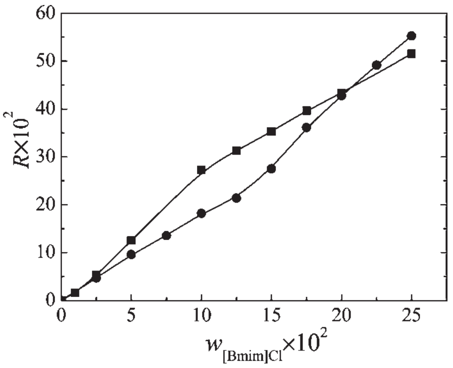

Figure 2. Comparison of salting-out ratio R of [Bmim]Cl on KCl and NaCl as a function of mass fraction of [Bmim]Cl w_1 in [Bmim]Cl(1) + H_2O (2) at T = 298.15 K. Symbols: ■, KCl; ●, NaCl.

Potassium sulfate (K_2SO_4) is used to produce multicomponent fertilizers, free of chlorine, and it is always applied widely in the agriculture. Currently, the main approach to produce potassium sulfate in the chemical industry is utilizing the double decomposition reaction of KCl and phosphogypsum. Experiments show that once the decomposition reaction occurs under the circumstances of ammonia, methanol, isopropanol, and so on the product efficiency in the process would have a greater improvement.[31−33] The ammonia and alcohol aqueous solutions influence the crystallization zone of K_2SO_4 in the phase diagram of the K^+, Ca^{2+}/Cl^-, SO_4^{2-} + H_2O system. An effective way of potassium sulfate production via double decomposition of gypsum and potassium chloride is increasing the concentration of ammonia and alcohols to increase the utilization coefficient of KCl. The process is potentially environmentally hazard due to their high volatility. ILs could be a suitable replacement for ammonia because of the following unique features. First, the use of ILs may be environmentally beneficial due to their negligible volatility. Second, to a limit, IL without its crystallization in a wider temperature is easy to use during the crystallization process of final products. Finally, the solution characteristic is easy to adjust by changing the cation or anion of ILs.

Calculated Results. Considering the solubility product K_{sp} is an equilibrium constant (regardless of whether the solution is a single or mixed electrolyte), the K_{sp} obtained in pure water could be applied directly to calculate the salt solubilities in the mixed electrolyte solutions. The K_{sp} is a function of the solubility and mean activity coefficient

$$\ln K_{sp} = \nu_M \ln(m_M) + \nu_X \ln(m_X) + \nu \ln \gamma_\pm \qquad (15)$$

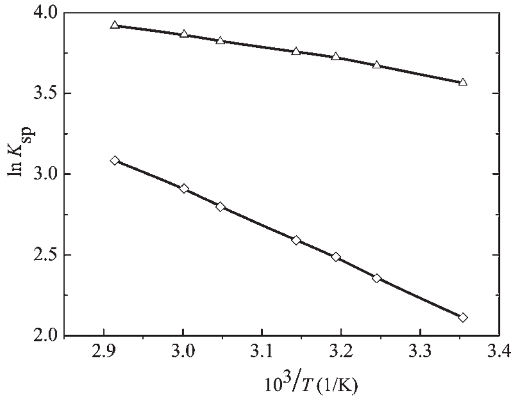

Figure 3. ln K_{sp} of KCl and NaCl in pure water as a function of the reciprocal of temperature $10^3/T$ (1/K). Symbols: ◇, KCl; △,NaCl.

Table 4. Correlated Ion Interaction Parameters Φ and Ψ of the Extended Pitzer Model at Different Temperatures T = (298.15 to 343.15) K

parameter	298.15 K	308.15 K	313.15 K	318.15 K	328.15 K	333.15 K	343.15 K
			KCl + H_2O + [Bmim]Cl				
$\Phi_{K,[\mathrm{Bmin}]}$	0.93200	0.88874	0.88063	0.87203	0.86885	0.86688	0.82018
$\Psi_{K,[\mathrm{Bmin}],Cl}$	1.4752	1.41682	1.39678	1.39272	1.38994	1.3605	1.23263
			NaCl + H_2O + [Bmim]Cl				
$\Phi_{Na,[\mathrm{Bmin}]}$	0.95347	1.03508	1.05328	1.06314	1.06378	1.06823	1.03555
$\Psi_{Na,[\mathrm{Bmin}],Cl}$	−0.08585	−0.104638	−0.11105	−0.11183	−0.10845	−0.01077	−0.10368

For single electrolytes of MX stoichiometry, the mean activity coefficients can be calculated by the Pitzer model[15]

$$\ln \gamma_{\pm} = |Z_M Z_X| f' + m(2\nu_M \nu_X/\nu) B_{MX} + m^2 \left[\frac{2(\nu_M \nu_X)^{3/2}}{\nu}\right] C_{MX} \tag{16}$$

and

$$\nu = \nu_M + \nu_X \tag{17}$$

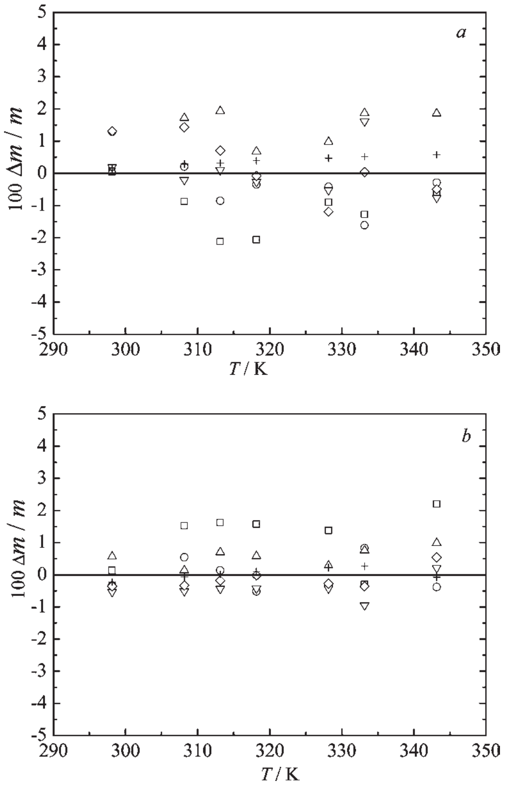

Figure 4. Fractional deviations $\Delta m = m(\text{exptl}) - m(\text{calcd})$ of the experimental solubilities $m(\text{exptl})$ of KCl (a) and NaCl (b) in [Bmim]Cl (1) + H_2O (2) from w_1 = (0 to 0.25) from values $m(\text{calcd})$ obtained with the extended Pitzer model as function of temperature. Symbols: □, w_1 = 0.25; ○, w_1 = 0.20; △, w_1 = 0.15; ▽, w_1 = 0.10; ◇, w_1 = 0.05; +, w_1 = 0.

For KCl and NaCl, the calculated K_{sp} value in pure water according to the model parameters and experimental solubilities shows a linear relation between ln K_{sp} and reciprocal temperature, as shown in Figure 3. At 298.15 K, the calculated ln K_{sp} for KCl and NaCl are 2.08 and 3.65, respectively, close to the value 2.06 and 3.63 reported by Christomir.[25]

With the solubility products K_{sp} of KCl and NaCl, θ_{MN} and Ψ_{MNX} in the modified Pitzer model were fitted using the given parameters in Table 1 as well as the experimental solubilities. All the model parameters regressed are listed in Table 4. The solubilities of KCl and NaCl in [Bmim]Cl + H_2O can then be calculated by the modified Pitzer model. A comparison between the experimental and the calculated results is shown in Figure 1, in which points represent the experimental results and solid lines denote calculated ones, respectively. The fractional deviation of the experimental solubilities from values obtained with the extended Pitzer model is shown in Figure 4. From the tables and figures, the calculated and experimental results are in good agreement, and the maximal absolute mean relative deviation is less than 0.012. These results indicate that the parameters obtained in this work are reliable and can be used to predict the solid−liquid equilibria at temperatures between (298.15 and 343.15) K and mass fractions of [Bmim]Cl up to 0.25.

Figure 5 plots the average activity coefficients, $\gamma_{\pm}$, for KCl and NaCl versus mass fraction of [Bmim]Cl in solution at (298.15, 313.15, and 333.15) K. Both $\gamma_{\pm(\text{KCl})}$ and $\gamma_{\pm(\text{NaCl})}$ increase with the addition of [Bmim]Cl, and $\gamma_{\pm}$ turns to be greater than 1 at the higher mass fraction of [Bmim]Cl. Average activity coefficients $\gamma_{\pm}$ greater than unity are also witnessed in other multicomponent systems.[34] Due to the constancy of K_{sp} at a given temperature, the increase of $\gamma_{\pm}$ means the decrease of solubilities of KCl and NaCl. The origin of the salt-out effect can be partly explained by the "common ion" effect. Taking 1−1 type [Bmim]Cl + NaCl mixed electrolyte solution as an example and supposing electrolytes are fully dissociable into the free ionic states for both [Bmim]Cl and NaCl, if $\gamma_{\pm} = 1$, because of $K_{sp} \approx m_{Na^+} \cdot m_{Cl^-} = m_{NaCl} \cdot (m_{NaCl} + m_{[Bmin]Cl})$, m_{NaCl} should decrease also along with the addition of [Bmim]Cl. This means that the presence of ILs promotes the precipitation of salts and inevitably leads to a lower solubility of NaCl. If $\gamma_{\pm} > 1$, the decrease of the solubility of inorganic salt with the addition of ILs will be even more prominent.

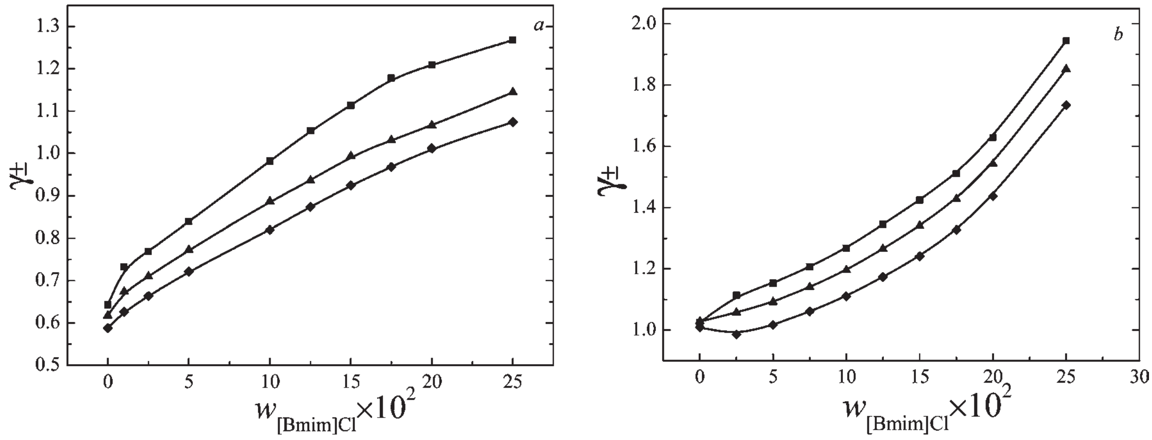

Figure 5. Average activity coefficient ln $\gamma_{\pm}$ of KCl (a) and NaCl (b) in the aqueous solutions [Bmim]Cl + H_2O with respect to mass fraction of [Bmim]Cl, $w_{[\text{Bmim}]\text{Cl}}$, in water at 298.15 K, 313.15 K, and 333.15 K. Symbols: ♦, T = 298.15 K; ▲, T = 313.15 K; ■, T = 333.15 K.

CONCLUSIONS

In this work, we presented the solubility data of KCl and NaCl in the aqueous system containing ionic liquid [Bmim]Cl in the temperature range of (298.15 to 343.15) K. Experimentally, the solubilities of KCl in [Bmim]Cl + H_2O increase more with temperature than the solubility of NaCl in [Bmim]Cl + H_2O. The addition of [Bmim]Cl leads to salting-out effects, markedly decreasing the salt solubility in the aqueous solution. Between $w_{[\mathrm{Bmim}]\mathrm{Cl}}$ = (0.025 to 0.20), the salting-out ratio of KCl and NaCl deviates, which indicates the possibility of their separation. The Pitzer model modified by Harvie and Weare was applied to correlate the experimental data. It was found that the calculated and experimental results are in good agreement, and the maximal absolute mean relative deviation is less than 0.012. These results indicate that the parameters obtained in this work are reliable and can be used to predict the solid−liquid equilibria over the temperature and IL fraction range of the experimental measurement. Further investigations of the influence of ILs in aqueous systems containing multiple inorganic salts are ongoing.

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Funding Sources

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (Nos. 20776040, 20876041, and 20736002), the National Basic Research Program of China (2009CB219902), the Program for Changjiang Scholars and Innovative Research Team in University of China (Grant IRT0721), and the 111 Project (Grant B08021) of China.

REFERENCES

(1) MacFarlane, D. R.; Seddon, K. R. Ionic Liquids—Progress on the Fundamental Issues. *Aust. J. Chem.* **2007**, *60*, 3–5.

(2) Pandy, S. Analytical Applications of Room-temperature Ionic Liquids: A Review of Recent Efforts. *Anal. Chim. Acta* **2006**, *556*, 38–45.

(3) Fadeev, A. G.; Meagher, M. M. Opportunities for Ionic Liquids in Recovery of Biofuels. *Chem. Commun.* **2001**, 3, 295–296.

(4) Bösmann, A.; Datsevich, L.; Jess, A. Deep Desulfurization of Diesel Fuel by Extraction with Ionic Liquids. *Chem. Commun.* **2001**, *23*, 2494–2495.

(5) Plechkova, N. V.; Seddon, K. R. Applications of Ionic Liquids in the Chemical Industry. *Chem. Soc. Rev.* **2008**, *37*, 123–150.

(6) Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H. How Ionic Are Room-Temperature Ionic Liquids? An Indicator of the Physicochemical Properties. *J. Phys. Chem. B* **2006**, *110*, 19593–19600.

(7) Earle, M. J.; Esperanca, J. M. S. S.; Gilea, M. A. The Distillation and Volatility of Ionic Liquids. *Nature* **2006**, *439*, 831–834.

(8) Wagner, M.; Stanga, O.; Schröer, W. Corresponding States Analysis of the Critical Points in Binary Solutions of Room Temperature Ionic Liquids. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3943–3950.

(9) Bridges, N. J.; Gutowski, K. E.; Rogers, R. D. Investigation of Aqueous Biphasic Systems formed from Solutions of Chaotropic Salts with Kosmotropic Salts (Salt−Salt ABS). *Green Chem.* **2007**, *9*, 177–183.

(10) Pei, Y.; Wang, J.; Liu, L.; Wu, K.; Zhao, Y. Liquid-Liquid Equilibria of Aqueous Biphasic Systems Containing Selected Imidazolium Ionic Liquids and Salts. *J. Chem. Eng. Data* **2007**, *52*, 2026–2031.

(11) Dupont, J.; Consorti, C. S. ; Suarez, P. A. Z.; Souza, R. F. *Inorganic Syntheses*; Hegedus, L. S., Ed.; John Wiley: Chichester, U.K. 2002; Vol. 79, p 236.

(12) Gutowski, K. E.; Broker, G. A.; Willauer, H. D. Controlling the Aqueous Miscibility of Ionic Liquids: Aqueous Biphasic Systems of Water-Miscible Ionic Liquids and Water-Structuring Salts for Recycle, Metathesis, and Separations. *J. Am. Chem. Soc.* **2003**, *125*, 6632–6633.

(13) Trindade, J. R.; Visak, Z. P.; Blesic, M. Salting-Out Effects in Aqueous Ionic Liquid Solutions: Cloud-Point Temperature Shifts. *J. Phys. Chem. B* **2007**, *111*, 4737–4741.

(14) Najdanovic-Visak, V.; Canongia, L. J. N.; Visak, Z. P.; Trindade, J.; Rebelo, L. P. N. Salting-out in Aqueous Solutions of Ionic Liquids and K_3PO_4: Aqueous Biphasic Systems and Salt Precipitation. *Int. J. Mol. Sci.* **2007**, *8*, 736–748.

(15) Freire, M. G.; Neves, C. M. S. S.; Silva, A. M. S. ^{1}H NMR and Molecular Dynamics Evidence for an Unexpected Interaction on the Origin of Salting-In/Salting-Out Phenomena. *J. Phys. Chem. B* **2010**, *114*, 2004–2014.

(16) Harvie, C. E.; Møller, N.; Weare, J. H. The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O System to High Ionic Strengths at 25°C. *Geochim. Cosmochim. Acta* **1984**, *48*, 723–751.

(17) Harvie, C. E.; Weare, J. E. The Predication of Mineral Solubilities in Nature Water: The Na-K-Mg-C1-SO_4-H_2O System from Zero to High Concentration at 25 °C. *Geochim. Cosmochim. Acta* **1980**, *44*, 981–996.

(18) Paul, A.; Mandal, P. K.; Samanta., A. On the Optical Properties of the Imidalium Ionic Liquids. *J. Phys. Chem. B* **2005**, *109*, 9148–9153.

(19) Pitzer, K. S. Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **1973**, *77*, 268–277.

(20) Moiler, N. The Prediction of Mineral Solubilities in Natural Waters: A Chemical Model for the Na-Ca-Cl-SO_4-H_2O System, to High Temperatures and Concentrations. *Geochim. Cosmochim. Acta* **1988**, *52*, 821–837.

(21) Jimenez, Y. P.; Taboada, M. E.; Galleguillos, H. R. Solid−liquid equilibrium of K_2SO_4 in solvent mixtures at different temperatures. *Fluid Phase Equilib.* **2009**, *284*, 114–117.

(22) Dean, J. A. *Lange's Chemistry Handbook Version*, 15th ed.; McGraw-Hill: New York, 1999; Vol. 5, pp 17−20.

(23) Galleguillos, H. R.; Taboada, M. E.; Graber, T. A. Compositions, Densities, and Refractive Indices of Potassium Chloride + Ethanol + Water and Sodium Chloride + Ethanol + Water Solutions at (298.15 and 313.15) K. *J. Chem. Eng. Data* **2003**, *48* (2), 405–410.

(24) Pinho, S. P.; Macedo, E. A. Solubility of NaCl, NaBr, and KCl in Water, Methanol, Ethanol, and Their Mixed Solvents. *J. Chem. Eng. Data* **2005**, *50*, 29–32.

(25) Christomir, C. Thermodynamics of Formation of Double Salts and Mixed Crystals from Aqueous Solutions. *J. Chem. Thermodyn.* **2005**, *37*, 1036–1060.

(26) Silvester, L. F.; Pitzer, K. S. Thermodynamics of Electrolytes. 8. High-Temperature Properties, Including Enthalpy and Heat Capacity, with Application to Sodium Chloride. *J. Phys. Chem.* **1977**, *81*, 1822–1828.

(27) Holmes, H. F.; Mesmer, R. E. Thermodynamic Properties of Aqueous Solutlons of the Alkali Metal Chlorides to 250°C. *J. Phys. Chem.* **1983**, *87*, 1242–1255.

(28) Shekaari, H.; Mousavi, S. S. Osmotic Coefficients and Refractive Indices of Aqueous Solutions of Ionic Liquids Containing 1-Butyl-3-methylimidazolium Halide at T = (298.15 to 328.15) K. *J. Chem. Eng. Data* **2009**, *54*, 823–829.

(29) González, B.; Calvar, N.; Domínguez, A.; Macedo, E. A. Osmotic Coefficients of Aqueous Solutions of Four Ionic Liquids at T = (313.15 and 333.15) K. *J. Chem. Thermodyn.* **2008**, *40*, 1346–1351.

(30) Grover, P. K.; Ryall, R. L. Critical Appraisal of Salting-Out and It Implications for Chemical and Biological Sciences. *Chem. Rev.* **2005**, *105*, 1–8.

(31) Fernandez, L. J. A.; Wint, A. Double Decomposition of Gypsum and Potassium Chloride Catalysed by Aqueous Ammonia. *Chem. Eng. J.* **1982**, *23*, 53.

(32) Samir, I. A.; Ali, A. B.; Mamdouh, A. A. K_2SO_4 production via the double decomposition reaction of KCl and phosphogypsum. *Chem. Eng. J.* **2000**, *76*, 197–207.

(33) Agnieszka, M.; Barbara, G.; Maria, T. Production of potassium sulfate from potassium hydrosulfate solutions using alcohols. *Chem. Pap.* **2008**, *62*, 123–126.

(34) Dinane, A.; Guendouzi, M. E.; Mounir, A. Hygrometric Determination of Water Activities, Osmotic and Activity Coefficients of (NaCl + KCl) (aq) at T = 298.15K. *J. Chem. Thermodyn.* **2002**, *34*, 423–441.