Liquid−Liquid Equilibria of the System 1-(2-Hydroxyethyl)-3-methylimidozolium Tetrafluoroborate or 1-(2-Hydroxyethyl)-2,3-dimethylimidozolium Tetrafluoroborate + Water + 1-Butanol at 293.15 K

Xuesheng Hu,[†,‡] Jiang Yu,*,[†] and Huizhou Liu*,[†]

Laboratory of Separation Science & Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100080, China, and Graduate School of Chinese Academy of Sciences, Beijing, 100039, China

Liquid−liquid equilibrium data are presented for mixtures of 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([C_2OHmim]BF_4) or 1-(2-hydroxyethyl)-2,3-dimethylimidazolium tetrafluoroborate ([C_2OHdmim]BF_4) + water + 1-butanol at 293.15 K. The data presented provide valuable insight into how the environmentally friendly ionic liquid solvent can be used to separate 1-butanol and water. Selectivity values, derived from the tie line data, show that [C_2OHdmim]BF_4 has better extraction capacity than [C_2OHmim]BF_4. The experimental results show that the two ionic liquids are potentially candidates to separate 1-butanol and water by liquid−liquid extraction. The experimental tie lines were correlated with the NTRL equation.

Introduction

The use of organic solvents in process operations leads to many problems (e.g., the main one concerning their toxicity for both the process operator and the environment and due to their volatility and flammable nature, which are also of importance for their transport and storage). Recently, room-temperature ionic liquids (RTILs) have emerged and are gaining academic and industrial attention in catalysis, separation processes, and electrochemistry as replacements for VOCs due to their particular properties.[1,2]

RTILs have been applied to separate some organic mixtures due to their negligible vapor pressure. Letcher and co-workers[3−6] used 1-hexyl-3-methylimidozolium tetrafluoroborate ([C_6mim]-BF_4), 1-hexyl-3-methylimidozolium hexafluorophosphate ([C_6-mim]PF_6), and 1-octyl-3-methylimidazolium chloride ([C_8mim]-Cl) to separate benzene, methanol, or ethanol from hexadecane, dodecane, heptane, 1-hexene, or 1-heptene. Arce et al.[7,8] separated an ethanol and *tert*-amyl ethyl ether mixture by 1-octyl-3-methylimidazolium chloride ([C_8mim]Cl) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim]Tfo). Selvan et al.[9] also measured liquid−liquid equilibria of 1-ethyl-3-methylimidazolium triiodide ([emim]I_3) or 1-butyl-3-methylimidazolium triiodide ([bmim]I_3), toluene, and heptane. All ionic liquids used above have good extraction efficiency according to the results, which shows that they are potential candidates to separate organic mixture by liquid−liquid extraction.

RTILs as a novel kind of materials to separate some organic−water systems were reported recently. Rogers and co-workers[10] reported liquid−liquid equilibria of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6), water, and ethanol. But they found that the existance of [bmim]PF_6 in liquid phase did not vary the vapor−liquid equilibria of ethanol to water. Arlt and co-workers[11,12] first reported that three ionic liquids (1-ethyl-3-methylimidazolium tetrafluoroborate ([emim]BF_4), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4), and 1-butyl-3-methylimidazolium chloride ([bmim]Cl)) can improve the relative volatility of ethanol to water. They also measured liquid−liquid equilibria of tetrahydrofuran (THF), water, and two ionic liquids ([emim]BF_4 and [bmim]BF_4). The results showed that the two ionic liquids had little solubility in THF. Although there was a large amount of THF (30 % mol fraction) in ionic liquids, which means unsatisfactory for practical extraction purposes to extract little water from THF and water azeotropic system. And they mentioned that changing the structure of ionic liquids such as enlarging the cation's alkyl chain can abate the miscibility gap between ionic liquids and THF. It will be very hopeful to meet the requirements concerning applications in the field of solvent extraction after optimizing the ILs selectivity.

The literatures above used mainly *N*,*N*-dialkyimidazolium ionic liquids, and ionic liquids with other functional groups are less studied. Branco et al.[13] first synthesized ionic liquids with hydroxyl and ether groups. Rogers and co-workers[14] found that the ionic liquids with hydroxyl group can form biphasic systems with acetone, which is quite different from *N*,*N*-dialkyimidazolium ionic liquids preciously reported. This means that ionic liquids with functional groups may have some special properties.

In the antibiotics industry, 1-butanol is a common solvent for crystallization of antibiotics such as Penicillin G. Before reuse, the water content in 1-butanol must be reduced from 80 % mass fraction to 1 to 2 % mass fraction. Azeotropic distillation and freezing-drying are generally used to remove water from 1-butanol + water mixture, which are both high energy-consuming processes.[15] A process with low energy-consuming and high selectivity is being studied such as membrane or liquid−liquid extraction by ionic liquids.

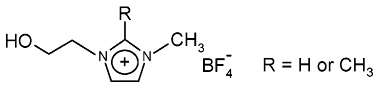
This work aims to elucidate the suitability of functionalized ionic liquids as extraction solvents for liquid−liquid extraction. Two ionic liquids with hydroxyl group are studied in this paper, their structures are shown in Scheme 1. The ternary liquid−liquid equilibria of the system 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate or 1-(2-hydroxyethyl)-2,3-dimeth-

---

* Corresponding authors. E-mail: jyu@home.ipe.ac.cn (J.Y.) or hzliu@home.ipe.ac.cn (H.L.). Fax: +8610-62554264.
[†] Chinese Academy of Sciences.
[‡] Graduate School of Chinese Academy of Sciences.

10.1021/je050455+ CCC: $33.50

Scheme 1. Structure of Ionic Liquids



ylimidazolium tetrafluoroborate + water + 1-butanol at 293.15 K is presented. The abilities of the two ionic liquids for separation of 1-butanol and water system are discussed.

Experimental Section

Materials. 1-Butanol, 2-chloroethanol, and $NaBF_4$ were all analytical grade reagents supplied by Beijing Chemical Reagents Corporation. 1-Methylimidazole was purchased from Kaile Chemical Plant (Linhai, Zhejiang, China) and distilled before use. 1,2-Dimethylimidazole was purchased from Suzhou Meihua Daily Use Perfume Company (Suzhou, Jiangsu, China).

1-(2-Hydroxyethyl)-3-methylimidazolium chloride ($[C_2OHmim]Cl$) or terafluoroborate ($[C_2OHmim]BF_4$) was synthesized by the methods described by Branco et al.[13] First, 2-chloroethanol (1.1 mol) and 1-methylimidazole (1.0 mol) were added to a round-bottomed flask fitted with a reflux condenser for 24 h at 333.15 K with stirring. The upper phase, containing unreacted starting materials, was decanted; the lower phase was washed with an equal volume of diethyl ether three times and then was under vacuum at 343.15 K for 8 h. The product, 1-(2-hydroxyethyl)-3-methylimidazolium chloride ($[C_2OHmim]Cl$), was a slightly yellow liquid (90 % yield). Second, $[C_2OHmim]Cl$ (0.5 mol) and $NaBF_4$ (0.55 mol) were mixed in 500 mL of acetone. The mixture was stirred at room temperature for 24 h. The resulting mixture was then filtered, the solvents were removed under vacuum at 343.15 K for 12 h to give the crude product, and over 95 % yield was obtained. Third, the crude ionic liquid including chloride impurity was diluted by a small amount of dichloromethane to lower the viscosity and filtered a couple of times by being passed through a silica column to remove chloride impurity analogous to the methods preciously reported.[16−19] The organic liquid phase obtained from the filtration method was tested for the residual chloride salt through the concentrated $AgNO_3$ solution, and no clear precipitation of AgCl was detected by the naked eye, which means that chloride impurity was almost adsorbed by silica. Dichloromethane was then removed under vacuum to give 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ($[C_2OHmim]BF_4$) as a colorless liquid ($\rho = 1.33$ g/mL, purity > 98.1 % mass fraction, water content < 1.9 % mass fraction determined by Karl Fischer method). Thus, the filtration method using silica column appears to be very effective in removing residual chloride ion. However, when purified, some loss of product will occur to result the overall yield was about 80 %.

Similarly, 1-(2-hydroxyethyl)-2,3-dimethylimidazolium chloride ($[C_2OHdmim]Cl$) or terafluoroborate ($[C_2OHdmim]BF_4$) was synthesized by using 1,2-dimethylimidazole instead of 1-methylimidazole. The ionic liquid $[C_2OHdmim]BF_4$ is also a colorless liquid ($\rho = 1.36$ g/mL, purity > 98.2 % mass fraction, water content < 1.8 % mass fraction).

Procedure. The ternary liquid−liquid equilibria $[C_2OHmim]BF_4$ (1) or $[C_2OHdmim]BF_4$ (1) + water (2) + 1-butanol (3) at 293.15 K was measured by the shake-flask method. The three materials were added into a jacketed glass vessel containing a magnetic stirrer connected to a temperature-controlled circulating bath. The mixture was stirred for 4 h and then put into a jacketed funnel connected to the same temperature-controlled circulating bath to settle for 20 h to achieve phase equilibria. All the temperatures were controlled to (293.15 ± 0.1) K.

The concentrations of ionic liquid of the upper and the lower phases were determined by a UV method (Perkin-Elmer Lambda Bio40 UV/Vis spectrometer at 210 nm). For example, 1 mL of liquid in the upper phase by recording the exact weight (m) was put into a 50 mL bottle. After evaporation under vacuum overnight to remove volatiles, the residual of ionic liquid is very small. About 30 mL of deionized water was put into the bottle to dilute the ionic liquid. The mixture was then removed to a 500 mL volumetric flask. This process was repeated at least 10 times to ensure that the residue of ionic liquid was almost washed off. Deionized water was finally added to the volumetric flask for the calibration tail. In general, the concentration of

Table 1. Tie Line Data of $[C_2OHmim]BF_4$ (1) + Water (2) + 1-Butanol (3) at 293.15 K

	1-butanol-rich phase			ionic liquid-rich phase				
no.	IL ($100\,w_1$)	water ($100\,w_2$)	1-butanol ($100\,w_3$)	IL ($100\,w_1$)	water ($100\,w_2$)	1-butanol ($100\,w_3$)	β	S
1	1.23	1.95	96.82	82.51	7.44	10.05	5.81	36.76
2	1.45	5.08	93.47	65.05	17.78	17.17	3.57	19.05
3	1.53	6.22	92.25	57.55	25.22	17.23	3.41	21.71
4	1.71	8.83	89.46	50.08	35.34	14.58	2.85	24.56
5	1.83	12.12	86.05	39.90	47.91	12.19	2.42	27.90
6	1.84	14.23	83.93	33.79	54.92	11.29	2.22	28.69
7	1.59	15.19	83.22	29.85	59.57	10.58	2.16	30.85
8	1.32	16.84	81.84	19.82	69.46	10.72	2.06	31.49
9	1.06	17.14	81.80	12.85	76.51	10.64	2.07	34.32
10	0.56	18.94	80.50	7.44	83.13	9.43	1.97	37.47

Table 2. Tie Line Data of $[C_2OHdmmim]BF_4$ (1) + Water (2) + 1-Butanol (3) at 293.15 K

	1-butanol-rich phase			ionic liquid-rich phase				
no.	IL ($100\,w_1$)	water ($100\,w_2$)	1-butanol ($100\,w_3$)	IL ($100\,w_1$)	water ($100\,w_2$)	1-butanol ($100\,w_3$)	β	S
1	1.83	1.41	96.76	89.21	8.35	2.44	5.92	234.84
2	6.21	6.23	87.56	74.89	18.30	6.81	2.94	37.77
3	6.07	9.49	84.44	65.17	27.85	6.98	2.94	35.50
4	5.52	10.43	84.05	57.00	35.77	7.23	3.43	39.87
5	5.34	13.18	81.48	48.74	44.40	6.86	3.37	40.01
6	4.66	14.06	81.28	40.15	54.33	5.52	3.86	56.90
7	3.48	15.35	81.17	29.57	65.37	5.06	4.26	68.31
8	2.72	16.46	80.82	18.18	76.89	4.93	4.67	76.58
9	1.21	17.91	80.88	10.27	85.89	3.84	4.80	101.01

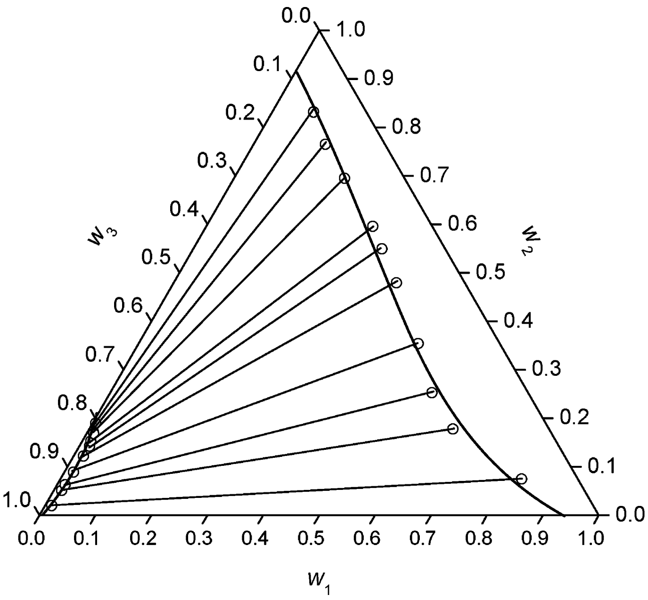


Figure 1. Ternary phase diagram of $[C_2OHmim]BF_4$ (1) + water (2) + 1-butanol (3) at 293.15 K.

ionic liquid in the 500 mL (V) volumetric flask is about from 20 mg·L^{-1} to 100 mg·L^{-1}. Due to the strong adsorption of ionic liquid to UV light, the ionic liquid sample with a concentration of about 30 mg/L will have an absorbance (A) of about 0.5. If the sample has an absorbance (A) of more than 0.95, the sample of ionic liquid needs to be further diluted to gain a lower concentration. The exact concentration (C) of sample was calculated by standard curve; the mass fraction of ionic liquid in ternary mixture was then calculated by the equation as follows:

$$w_1 = \frac{C \times V}{m}$$

The water content of the two phases was measured by Karl Fischer titration. The 1-butanol content was calculated by material balance as

$$w_3 = 1 - (w_1 + w_2)$$

Every tie line has been reproduced at least once. The mole fraction of each component can be determined within 2 %.

Results and Discussion

The $[C_2OHmim]BF_4$ (1) (or $[C_2OHdmim]BF_4$) + water (2) + 1-butanol (3) system has a liquid−liquid miscibility gap consisting of an upper 1-butanol-rich phase and a lower IL-rich phase. The compositions of the tie line data are presented in Table 1 for $[C_2OHmim]BF_4$) (1) + water (2) + 1-butanol (3) and in Table 2 for $[C_2OHdmim]BF_4$ (1) + water (2) + 1-butanol (3). The corresponding ternary phase diagram are shown as Figure 1 for $[C_2OHmim]BF_4$ (1) + water (2) + 1-butanol (3) and as Figure 2 for $[C_2OHdmim]BF_4$ (1) + water (2) + 1-butanol (3). The 1-butanol-rich phase contains only traces of $[C_2OHmim]BF_4$ (< 2 % mass fraction), and the solubility of 1-butanol in $[C_2OHmim]BF_4$ is about 7 % mass fraction. Similarly $[C_2OHdmim]BF_4$ has little solubility in 1-butanol (< 1.0 % mass fraction), but the $[C_2OHdmim]BF_4$ phase has about 3.0 % mass fraction of 1-butanol. The sloping of tie lines to the 1-butanol vertex in Figure 1 and Figure 2 is very clear.

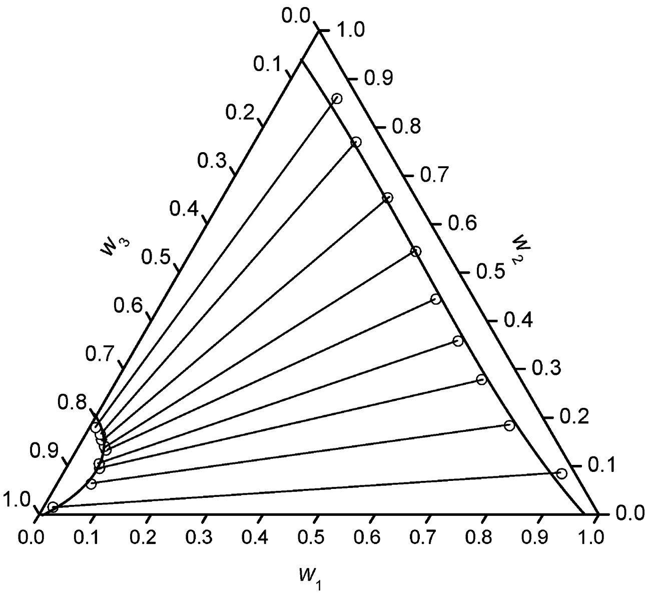


Figure 2. Ternary phase diagram of $[C_2OHmmim]BF_4$ (1) + water (2) + 1-butanol (3) at 293.15 K.

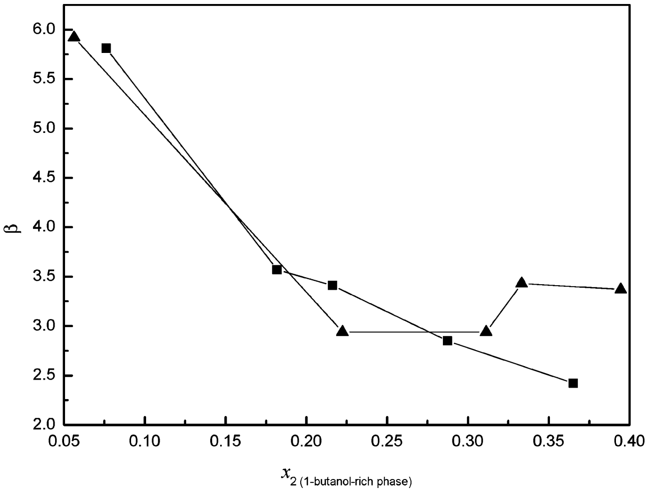


Figure 3. Comparison of the distribution ratio of water in different ionic liquids system: ■, as $[C_2OHmim]BF_4$; ▲, as $[C_2OHdmim]BF_4$. x_2 refers to the mole fraction of water in 1-butanol-rich phase.

The selectivity (S) and distribution ratio (β) are important parameters in assessing the feasibility of utilizing the solvent in liquid−liquid extraction. With regard to the 1-butanol + water mixture studied, the selectivity (S) of extracting water from the mixture and the distribution ratio (β) of water in two phases are given in terms of mole fraction as

$$S = \frac{(x_2/x_3)_{\text{ionic liquid−rich phase}}}{(x_2/x_3)_{\text{1−butanol−rich phase}}}$$

$$\beta = \frac{(x_2)_{\text{ionic liquid−rich phase}}}{(x_2)_{\text{1−butanol−rich phase}}}$$

The distribution ratio data show that the ionic liquid phase has commonly more water than the 1-butanol phase. As Figure 3 shows, the distribution ratio of water in different ionic liquids systems is unlike. When the water content in 1-butanol-rich phase rises, the distribution ratio of water in the $[C_2OHmim]BF_4$ system decreases, while the distribution ratio of water in the $[C_2OHdmim]BF_4$ system goes down first and then arises. When the water content in the 1-butanol-rich phase is low (x_1

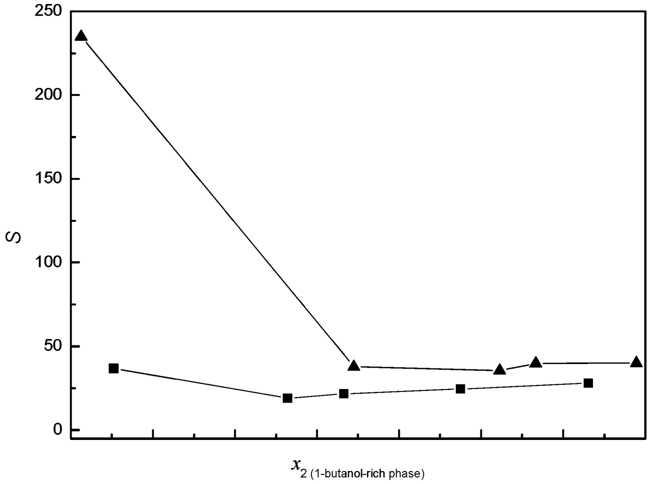


Figure 4. Comparison of selectivity of $[C_2OHmim]BF_4$ and $[C_2OHdmim]BF_4$: ■, as $[C_2OHmim]BF_4$; ▲, as $[C_2OHdmim]BF_4$. x_2 refers to the mole fraction of water in 1-butanol-rich phase.

< 0.20), the distribution ratio of water in different ionic liquids systems is almost the same.

The selectivity data show that $[C_2OHmim]BF_4$ and $[C_2OHdmim]BF_4$ have good efficiency to extract water from the 1-butanol and water mixture. As Figure 4 shows, the selectivities of the two ionic liquids are alike. When the water content in 1-butanol-rich phase rises, the selectivity of $[C_2OHmim]BF_4$ decreases, while the selectivity of $[C_2OHdmim]BF_4$ also goes down. When the water content in the 1-butanol-rich phase is low ($x_1 < 0.25$), the selectivity of $[C_2OHdmim]BF_4$ is much better than that of $[C_2OHmim]BF_4$.

Based on the four figures above, the two ionic liquids $[C_2OHmim]BF_4$ and $[C_2OHdmim]BF_4$ can be used for 1-butanol and water separation by solvent extraction. The addition of a 40 % mass fraction $[C_2OHmim]BF_4$ or $[C_2OHdmim]BF_4$ to a preconcetrated binary 1-butanol + water solution (such as 80 % mass fraction of 1-butanol) causes a phase split. For $[C_2OHmim]BF_4$, the upper phase contains about 93.9 % mass fraction of 1-butanol, 4.8 % mass fraction of water, and 1.3 % mass fraction of $[C_2OHmim]BF_4$. The lower phase consists of 15.0 % mass fraction of 1-butanol, 15.0 % mass fraction of water, and 70.0 % mass fraction of $[C_2OHmim]BF_4$. In the upper phase, the 1-butanol + water preliminary composition has been changed. Similarly for $[C_2OHdmim]BF_4$, the upper phase contains about 87.6 % mass fraction of 1-butanol, 6.2 % mass fraction of water, and 6.2 % mass fraction of $[C_2OHdmim]BF_4$. The lower phase consists of 7.0 % mass fraction of 1-butanol, 18.0 % mass fraction of water, and 75.0 % mass fraction of $[C_2OHdmim]BF_4$. In the upper phase, the 1-butanol + water preliminary composition is changed.

Compared with using VOCs, the use of ionic liquids to separate 1-butanol and water takes advantage of their no vapor pressure, being easily transported and reused. They have a similar "salting out" effect as some solid salts. The experimental results above show that the two ionic liquids are potential candidates to separate 1-butanol and water.

Tie Line Correlation

The nonrandom two-liquid equation (NTRL) by Renon and Prausnitz[20] was employed to correlate the experimental tie line data for the ternary systems investigated. Despite the fact that it is intended for nonelectrolyte solutions, a proper model for ionic liquids has not yet been developed for correlation and prediction purposes. Previous works used the NRTL equation to satisfactorily correlate LLE data.[3−10]

Table 3. Values of Parameters for the NRTL Equation for the Ternary Mixtures $\{[C_2OHmim]BF_4$ or $[C_2OHdmim]BF_4$ (1) + Water (2) + 1-Butanol (3)$\}$

component ($i - j$)	τ_{ij}		α	rmsd
$[C_2OHmim]BF_4$ (1) + Water(2) + 1-Butanol (3)				
1−2	0.191	1.596	0.20	0.010
1−3	7.622	13.217		
2−3	4.010	−0.144		
$[C_2OHdmim]BF_4$ (1) + Water (2) + 1-Butanol (3)				
1−2	0.321	2.003	0.20	0.009
1−3	7.783	15.196		
2−3	4.010	−0.144		

The NRTL equation for a solution of m components is

$$\ln \gamma_i = \frac{\sum_{j=1}^{m} x_j \tau_{ji} G_{ji}}{\sum_{k=1}^{m} x_k G_{ki}} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{k=1}^{m} x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{r=1}^{m} x_r G_{rj} \tau_{rj}}{\sum_{k=1}^{m} x_k G_{kj}} \right)$$

where

$$\tau_{ij} = \frac{(g_{ij} - g_{jj})}{RT}; \quad G_{ij} = \exp(-\alpha_{ij}\tau_{ij}); \quad (\alpha_{ij} = \alpha_{jj})$$

where g = the energy parameter, x = the mole fraction, α_{ij} = the nonrandomness parameter, γ = the activity coefficient, τ = the interaction parameter, and i, j, k = the component indices.

The objective function, OF, was used to minimize the difference between the experimental and calculated mole fraction compositions defined as

$$\mathrm{OF} = \sum_{k=1}^{n} \sum_{i=1}^{3} \sum_{j=1}^{2} \left[\frac{(x_{ijk}(\exp) - x_{ijk}(\mathrm{calc}))^2}{6n} \right]^{1/2}$$

The parameters that were calculated in this manner in the form of $g_{ij} - g_{jj}$ and $g_{ji} - g_{ii}$ for the NTRL equation are given in Table 3, together with the root-mean-square deviation (rmsd) values defined as

$$\mathrm{rmsd} = \{\sum_k [\sum_j (\sum_i (x_{i,\exp} - x_{i,\mathrm{calc}})^2)/6n]\}^{1/2}$$

where x is the mole fraction and the subscripts i, j, and k provide a designation for the component, the phase, and the tie line, respectively. The value n designates the number of interaction components.

The α value of 0.2 is commonly used.[21] The interaction parameters τ calculated are not quite different for $[C_2OHmim]BF_4$ and $[C_2OHdmim]BF_4$ because the two ionic liquids have similar structure and physical properties. The only little difference between the interaction parameters values may results from the fact that $[C_2OHdmim]BF_4$ has C_2-position CH_3 instead of C_2-position H. The hydrogen at the C_2-position of the imidazolium ring is known to be the most acidic hydrogen on the ring. Therefore, the cation can presumably form a hydrogen bond with the alcohol at this hydrogen.[22] By replacing the hydrogen of the $[C_2OHmim]$ cation with a methyl group (forming $[C_2OHdmim]$), the ability of the cation to hydrogen bond with 1-butanol is diminished, resulting in a decrease in the mutual solubility of the ionic liquid $[C_2OHdmim]BF_4$ and 1-butanol. Meanwhile this indirectly results in more water being extracted into the ionic liquid phase, which explains why $[C_2OHdmim]BF_4$ has a little better extraction capacity than $[C_2OHmim]BF_4$.

The $\tau_{23} = 4.010$, $\tau_{32} = -0.144$ calculated by the NRTL equation are approach to Li's results,[20] which means these values are credible. The rmsd values from Table 3 provide a measure of the accuracy of the correlation. As can be inferred from the rmsd values, fairly good correlation of the experimental values with the NTRL model was obtained.

Conclusions

Liquid−liquid equilibrium data were obtained for the ternary mixtures of $[C_2OHmim]BF_4$ or $[C_2OHdmim]BF_4$ + water + 1-butanol at 293.15 K. The extraction efficiencies of the two ionic liquids for the 1-butanol + water mixture were examined. The sloping of tie lines and selectivity data show clearly the two ionic liquids emerged as the favorable choice as a solvent for the separation of 1-butanol and water by liquid−liquid extraction.

Literature Cited

(1) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, Germany, 2003.
(2) Rogers, R. D.; Seddon, K. R. Ionic liquids—solvents of the future? *Science* **2003**, *302*, 792−793.
(3) Letcher, T. M.; Reddy, P. Ternary (liquid + liquid) equilibria for mixtures of 1-hexyl-3-methylimidazolium (tetrafluoroborate or hexafluorophosphate) + benzene + an alkane at $T = 298.2$ K and $p = 0.1$ MPa. *J. Chem. Thermodyn.* **2005**, *37*, 415−421.
(4) Letcher, T. M.; Reddy, P. Ternary liquid−liquid equilibria for mixtures of 1-hexyl-3-methylimidozolium (tetrafluoroborate or hexafluorophosphate) + ethanol + an alkene at $T = 298.2$ K. *Fluid Phase Equilib.* **2004**, *219*, 107−112.
(5) Letcher, T. M.; Deenadayalu, N. Ternary liquid−liquid equilibria for mixtures of 1-methyl-3-octyl-imidazolium chloride + benzene + an alkane at $T = 298.2$ K and 1 atm. *J. Chem. Thermodyn.* **2003**, *35*, 67−76.
(6) Letcher, T. M.; Deenadayalu, N.; Soko, B.; Ramjugernath, D.; Naicker, P. K. Ternary liquid−liquid equilibria for mixtures of 1-methyl-3-octylimidazolium chloride + an alkanol + an alkane at 298.2 K and 1 bar. *J. Chem. Eng. Data* **2003**, *48*, 904−907.
(7) Arce, A.; Rodriguez, O.; Soto, A. Experimental determination of liquid−liquid equilibrium using ionic liquids: *tert*-amyl ethyl ether + ethanol + 1-octyl-3-methylimidazolium chloride system at 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 514−517.
(8) Arce, A.; Rodriguez, O.; Soto, A. *tert*-Amyl ethyl ether separation from its mixtures with ethanol using the 1-butyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid: liquid−liquid equilibrium. *Ind. Eng. Chem. Res.* **2004**, *43*, 8323−8327.
(9) Selvan, M. S.; McKinley, M. D.; Dubois, R. H.; Atwood, J. L. Liquid−liquid equilibria for toluene + heptane + 1-ethyl-3-methylimidazolium triiodide and toluene + heptane + 1-butyl-3-methylimidazolium triiodide. *J. Chem. Eng. Data* **2000**, *45*, 841−845.
(10) Swatloski, R. P.; Visser, A. E.; Reichert, W. M.; Broker, G. A.; Farina, L. M.; Holbrey, J. D.; Rogers, R. D. On the solubilization of water with ethanol in hydrophobic hexafluorophosphate ionic liquids. *Green Chem.* **2002**, *4*, 81−87.
(11) Jork, C.; Seiler, M.; Beste, Y. A.; Arlt, W. Influence of ionic liquids on the phase behavior of aqueous azeotropic systems. *J. Chem. Eng. Data* **2004**, *49*, 852−857.
(12) Seiler, M.; Jork, C.; Kavarnou, A.; Arlt, W.; Hirsch, R. Separation of azeotropic mixtures using hyperbranched polymers or ionic liquids. *AIChE J.* **2004**, *50*, 2439−2454.
(13) Branco, L. C.; Rosa, J. N.; Moura Ramos, J. J.; Afonso, C. A. M. Preparation and characterization of new room-temperature ionic liquids. *Chem. Eur. J.* **2002**, *8*, 3671−3677.
(14) Holbrey, J. D.; Turner, M. B.; Reichert, W. M.; Rogers, R. D. New ionic liquids containing an appended hydroxyl functionality from the atom-efficient, one-pot reaction of 1-methylimidazole and acid with propylene oxide. *Green Chem.* **2003**, *5*, 731−736.
(15) Wu, X. Y.; Xiong, Z. G.; Hu, Z. Z. *Process in Antibiotics Industry*; Chinese Chemical Industry Press: 1987; pp 211−213.
(16) Park, S.; Kazlauskas, R. J. Improved preparation and use of room-temperature ionic liquids in lipase-catalyzed enantio- and regioselective acylations. *J. Org. Chem.* **2001**, *66*, 8395−8401.
(17) Billard, I.; Moutiers, G.; Labet, A.; El Azzi, A.; Gaillard, C.; Mariet, C.; Lutzenkirchen, K. Stability of divalent europium in an ionic liquid: spectroscopic investigations in 1-methyl-3-butylimidazolium hexafluorophosphate. *Inorg. Chem.* **2003**, *42*, 1726−1733.
(18) Yeon, S. H.; Kim, K. S.; Choi, S.; Lee, H.; Kim, H. S.; Kim, H. Physical and electrochemical properties of 1-(2-hydroxyethyl)-3-methyl imidazolium and *N*-(2-hydroxyethyl)-*N*-methyl morpholinium ionic liquids. *Electrochim. Acta* **2005**, *50*, 5399−5407.
(19) Paul, A.; Mandal, K. P.; Samanta, A. On the optical properties of the imidazolium ionic liquids. *J. Phys. Chem. B* **2005**, *109*, 9148−9153
(20) Renon, H.; Prausnitz, J. M. Local composition in thermodynamics excess function for liquid mixtures. *AIChE J.* **1968**, *14*, 135−144.
(21) Li, Z. C.; Tang, Y. P.; Liu, Y.; Li, Y. G. Salting effect in partially miscible systems of *n*-butanol−water and butanone−water 1. Determination and correlation of liquid−liquid equilibrium data. *Fluid Phase Equilib.* **1995**, *103*, 143−153.
(22) Crosthwaite, J. M.; Aki, S. N. V.; Maginn, E. J.; Brennecke, J. F. Liquid-phase behavior of imidazolium-based ionic liquids with alcohols: effect of hydrogen bonding and non-polar interactions. *Fluid Phase Equilib.* **2005**, *228*−*229*, 303−309.

Received for review October 26, 2005. Accepted January 13, 2006. We are thankful for the financial support from the National Natural Science Foundation of China (Grants 20221603 and 20490200).

JE050455+