J. Chem. Eng. Data **2008,** *53,* 427–433

Separation of Ethyl Acetate and Ethanol by Room Temperature Ionic Liquids with the Tetrafluoroborate Anion

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Liquid–liquid equilibrium data are presented for mixtures of 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim]BF_4) or 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([C_2OHmim]BF_4) or 1-ethyl-2,3-dimethylimidazolium tetrafluoroborate ([edmim]BF_4) or 1-(2-hydroxyethyl)-2,3-dimethylimidazolium tetrafluoroborate ([C_2OHdmim]BF_4) + ethanol + ethyl acetate at 298.15 K. The distribution ratio and selectivity values, derived from the tie line data, show that [C_2OHmim]BF_4 has better extraction capacity than other studied ionic liquids and that a hydroxyl group on the cation and a CH_3 group at the 2-position can obviously affect the interaction between the ionic liquid and ethanol. The experimental results show that [C_2OHmim]BF_4 is potentially a candidate to separate ethyl acetate and ethanol by liquid–liquid extraction. The experimental tie lines were correlated with the NRTL equation.

Introduction

Due to their measurable but relatively low vapor pressure, room-temperature ionic liquids have been applied to separate some organic mixtures.[1,2] Alrt et al.[3,4] reported that 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim]BF_4) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) can change the liquid–liquid equilibria of THF and water. Meindersma et al.[5] used 1-ethyl-3-methylimidazolium ethylsulfate ([emim]$C_2H_5SO_4$), 1,3-dimethylimidazolium methylsulfate ([mmim]CH_3SO_4), and 1-butyl-3-methylimidazolium methylsulfate ([bmim]CH_3SO_4) to separate toluene and *n*-heptane. Arce et al.[6] separated the hexane and benzene mixture by 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide ([C_2mim]NTf_2). All ionic liquids used above have good extraction efficiency according to the results, which shows that they are potentially candidates to separate organic mixtures by liquid–liquid extraction.

In many chemical processes, ester−alkanol systems need be separated to obtain pure ester and pure alkanol. For example, during acetic acid/ethanol esterification, about 9 % by mass of ethanol in the crude ethyl acetate product needs to be removed by a high-energy-consuming process such as extractive distillation.[7] Liquid–liquid extraction of ester−alkanol systems by ionic liquids, which may be a high selectivity process with low-energy consumption, was reported recently. Pereiro et al.[8] reported liquid–liquid equilibria of 2-propanol + ethyl acetate + 1,3-dimethylimidazolium methylsulfate ([mmim]CH_3SO_4) or 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) or 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim]PF_6), which showed that [mmim]CH_3SO_4 obtained higher values than [Rmim]PF_6 for the proposed process according to the selectivity values.

Recently, ionic liquids with functional hydroxyl groups have been studied to separate alcohols from other solvents.[9,10] In our previous work,[9] ionic liquids with a hydroxyl group were tried to separate 1-butanol and water, which also showed that the mutual solubility between alkanol and ionic liquids can be adjusted by changing the substituting group H or CH_3 at the C_2 position. This work continues to aim to elucidate the suitability of different ionic liquids as extraction solvents for liquid–liquid extraction. Four ionic liquids with the tetrafluoroborate anion are studied in this paper.

The ternary liquid–liquid equilibria of the system 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim]BF_4) or 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([C_2OHmim]BF_4) or 1-ethyl-2,3-dimethylimidazolium tetrafluoroborate ([edmim]BF_4) or 1-(2-hydroxyethyl)-2,3-dimethylimidazolium tetrafluoroborate ([C_2OHdmim]BF_4) + ethanol + ethyl acetate at 298.15 K is presented. The abilities of the four ionic liquids for separation of the ethyl acetate and ethanol system are discussed.

Experimental

Materials. Ethyl acetate, ethanol, 2-chloroethanol, ethyl bromide, and $NaBF_4$ were all analytical grade reagents (purity ≥ 99 %) supplied by Beijing Chemical Reagents Corporation. 1-Methylimidazole and 1,2-dimethylimidazole (purity ≥ 99 %) were purchased from Suzhou Meihua Daily Use Perfume Company (Suzhou, Jiangsu, China) and distilled before use.

1-Ethyl-3-methylimidazolium tetrafluoroborate ([emim]BF_4) was synthesized by the traditional method.[11,12] First, ethyl bromide (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 room temperature with stirring. Then, the temperature was allowed to rise to 343.15 K to remove unreacted ethyl bromide. The product was washed by ethyl ether three times and then was under a vacuum at 343.15 K for 8 h. The product, 1-ethyl-3-methylimidazolium bromide ([emim]Br), was solid at room temperature (90 % yield). Second, [emim]Br (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 a 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 bromide impurity was diluted by a small amount of dichloromethane to lower the viscosity and filtered a couple of

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10.1021/je700516t CCC: $40.75

Table 1. Physical Properties of the Pure Components at T = 298.15 K: Mole Mass M, Density ρ, and Water Mass Fraction w

	M (g·mol^{-1})	ρ(exptl) (g·cm^{-3})	ρ(lit.) (g·cm^{-3})	w (10^6)
[emim]BF_4	197.97	1.242	1.240[a]	55
[edmim]BF_4	212.00	1.250	–[b]	60
[C_2OHmim]BF_4	213.97	1.332	1.33[c]	80
[C_2OHdmim]BF_4	228.00	1.368	1.36[d]	89

[a] Ref 1. [b] No literature reported. [c] Ref 11. [d] Ref 9.

times by being passed through a silica column to remove the bromide impurity analogous to the methods previously reported.[13,14] The ionic liquid phase obtained from the filtration method was tested for the residual bromide salt through the concentrated $AgNO_3$ solution, and no clear precipitation of AgBr was detected by the naked eye, which means that bromide impurity was almost adsorbed by the silica. The dichloromethane was then removed under vacuum to give the 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim]BF_4) as a colorless liquid (purity > 99.0 % mass fraction, water content < 1.0 % mass fraction). Thus, the filtration method using a silica column appears to be very effective in removing the residual bromide ion. However, when purified, some loss of product will occur, resulting in an overall yield of about 80 %.

Similarly, the other three ionic liquids, 1-ethyl-2,3-dimethylimidazolium terafluoroborate ([edmim]BF_4, purity > 99.0 % mass fraction, water content < 1.0 % mass fraction), 1-(2-hydroxyethyl)-3-methylimidazolium terafluoroborate ([C_2OHmim]BF_4, purity > 99.0 % mass fraction, water content < 1.0 % mass fraction), and 1-(2-hydroxyethyl)-2,3-dimethylimidazolium tetrafluoroborate ([C_2OHdmim]BF_4, purity > 99.0 % mass fraction, water content < 1.0 % mass fraction) were synthesized by using 1,2-dimethylimidazole instead of 1-methylimidazole or 2-chloroethanol instead of ethyl bromide. The four ionic liquids used in this work have a purity of more than 99 % mass fraction and a water content less than 1 % mass fraction determined by the Karl Fischer method (SC-6 mini-amount Water Detective Instrument, Shangdong Zhonghui Instrument Company, 5 mg of H_2O·cm^{-3}).

Before use, every sample of ionic liquid was heated at 333.15 K for 24 h under reduced pressure to remove residual water. The physical properties of these ionic liquids at T = 298.15 K and water content before use were listed in Table 1.

Procedure. The binodal curves were determined at T = 298.15 K and 101.325 kPa through the use of the cloud-point titration technique described by Letcher and Siswana.[15] All mixtures were prepared and "titrated" in screwcap glass vials with septa to allow for careful sampling with glass syringes. The glass vial has a diameter of 2 cm, a height of 10 cm, and a total capacity of about 10 cm^3. There was negligible mass loss from the glass vials.

The determination of the tie line compositions was carried out by correlating the densities of the two immiscible liquid phases of the conjugate solutions with that of standard curves of density versus composition for the three components. The standard curve was obtained by measuring the densities of binary mixtures of ethyl acetate and ethanol and equilibrium ternary mixtures of the components, i.e., at the cloud-point, throughout the composition range of the ternary system. The density values of each conjugate phase, i.e., two phases, in the ternary mixture were then correlated with the standard curve to obtain the compositions of the components in each of the phases. Only two of the three component compositions are required for each phase, as the third is obtained by subtracting the sum of the other two from a value of 1; e.g., after measuring the densities of the upper and lower phases at equilibrium point, we can calculate the actual compositions of w_1 and w_2 by the interpolation method according to the standard curve determined by cloud-point titration and get w_3 with $1-w_1-w_2$.

Table 2. Solubility Data for [emim]BF_4 (1) + Ethanol (2) + Ethyl Acetate (3) at T = 298.15 K

x_1	x_2	x_3	ρ/g·cm^{-3}
0.655	0.000	0.345	1.112
0.536	0.102	0.361	1.080
0.465	0.155	0.379	1.071
0.401	0.219	0.380	1.058
0.351	0.249	0.400	1.021
0.312	0.276	0.411	1.006
0.267	0.300	0.434	0.999
0.255	0.307	0.438	0.997
0.239	0.314	0.447	0.984
0.209	0.327	0.464	0.968
0.182	0.336	0.481	0.954
0.155	0.337	0.508	0.932
0.127	0.337	0.536	0.896
0.110	0.331	0.559	0.894
0.091	0.324	0.584	0.892
0.077	0.315	0.608	0.890
0.064	0.301	0.636	0.888
0.047	0.265	0.688	0.886
0.039	0.241	0.721	0.885
0.028	0.230	0.742	0.882
0.017	0.208	0.775	0.870
0.013	0.165	0.823	0.864
0.006	0.111	0.882	0.828
0.002	0.056	0.942	0.819

The densities were measured through the use of a calibrated Anton Paar DMA 5000 density meter with an uncertainty of $1 \cdot 10^{-4}$ g·cm^{-3} in the measurement.

The ternary liquid–liquid equilibrium [emim]BF_4 (1) or [edmim]BF_4 (1) or [C_2OHmim]BF_4 (1) or [C_2OHdmim]BF_4 (1) + ethanol (2) + ethyl acetate (3) at 298.15 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 (501A Super Constant Temp Bath, Shanghai Hengping Instrument Company, ± 0.1 K). The mixture was stirred and then put into a jacketed funnel connected to the same temperature-controlled circulating bath to settle for 24 h to achieve phase equilibrium. All the temperatures were controlled to (298.15 ± 0.1) K.

Every tie line has been reproduced at least once. The mole fraction of each component can be determined with an uncertainty of ⩽ 0.2 %.

Results and Discussion

The compositions of the solubility curve data for [emim]BF_4 (1) + ethanol (2) + ethyl acetate (3), [C_2OHmim]BF_4 (1) + ethanol (2) + ethyl acetate (3), [edmim]BF_4 (1) + ethanol (2) + ethyl acetate (3), and [C_2OHdmim]BF_4 (1) + ethanol (2) + ethyl acetate (3) are presented in Tables 2 to 5, respectively, and the corresponding solubility curve diagrams are also shown as Figures 1 to 4, respectively. As shown in Figures 1 to 4, all the studied ILs have low solubility in ethyl acetate (< 1 % mole fraction), except [edmim]BF_4 which has about 6 % mole fraction. The solubility of ethyl acetate is (35, 21, 40, and 30) % mole fraction, respectively, in [emim]BF_4, [C_2OHmim]BF_4, [edmim]BF_4, and [C_2OHdmim]BF_4.

The compositions of the tie line data for [emim]BF_4 (1) + ethanol (2) + ethyl acetate (3), [C_2OHmim]BF_4 (1) + ethanol (2) + ethyl acetate (3), [edmim]BF_4 (1) + ethanol (2) + ethyl acetate (3), and [C_2OHdmim]BF_4 (1) + ethanol (2) + ethyl

Table 3. Solubility Data for $[C_2OHmim]BF_4$ (1) + Ethanol (2) + Ethyl Acetate (3) at T = 298.15 K

x_1	x_2	x_3	$\rho/g \cdot cm^{-3}$
0.784	0.000	0.216	1.205
0.637	0.157	0.206	1.172
0.493	0.302	0.205	1.154
0.409	0.397	0.194	1.133
0.332	0.468	0.200	1.102
0.284	0.512	0.204	1.050
0.258	0.534	0.208	1.028
0.217	0.570	0.213	1.019
0.185	0.591	0.225	1.011
0.154	0.600	0.246	1.008
0.131	0.608	0.261	0.997
0.108	0.609	0.283	0.953
0.085	0.601	0.314	0.899
0.064	0.577	0.359	0.873
0.052	0.556	0.391	0.870
0.039	0.530	0.431	0.865
0.036	0.499	0.466	0.855
0.028	0.475	0.497	0.850
0.022	0.444	0.534	0.849
0.015	0.404	0.581	0.845
0.011	0.381	0.608	0.842
0.011	0.350	0.638	0.837
0.010	0.325	0.665	0.830
0.009	0.291	0.701	0.828
0.008	0.264	0.727	0.824
0.007	0.224	0.769	0.821
0.005	0.152	0.844	0.817
0.004	0.116	0.880	0.811
0.002	0.063	0.935	0.805

Table 4. Solubility Data for $[edmim]BF_4$ (1) + Ethanol (2) + Ethyl Acetate (3) at T = 298.15 K

x_1	x_2	x_3	$\rho/g \cdot cm^{-3}$
0.602	0.000	0.398	1.070
0.510	0.077	0.414	1.066
0.477	0.108	0.415	1.016
0.442	0.133	0.424	1.032
0.411	0.162	0.427	1.030
0.385	0.180	0.435	1.028
0.360	0.208	0.432	1.015
0.316	0.249	0.435	1.004
0.291	0.268	0.441	0.985
0.267	0.292	0.442	0.966
0.247	0.306	0.447	0.954
0.226	0.325	0.448	0.951
0.212	0.336	0.452	0.944
0.194	0.348	0.459	0.927
0.178	0.356	0.466	0.915
0.161	0.363	0.476	0.898
0.151	0.367	0.482	0.884
0.137	0.375	0.488	0.881
0.126	0.376	0.498	0.878
0.115	0.376	0.509	0.875
0.104	0.376	0.520	0.872
0.094	0.370	0.537	0.867
0.080	0.358	0.562	0.858
0.066	0.349	0.585	0.855
0.062	0.329	0.609	0.852
0.057	0.300	0.643	0.851
0.057	0.267	0.676	0.849
0.055	0.244	0.701	0.847
0.055	0.202	0.743	0.846
0.054	0.164	0.782	0.845
0.057	0.083	0.860	0.843
0.055	0.132	0.814	0.842
0.057	0.056	0.887	0.834
0.058	0.000	0.942	0.822

acetate (3) are presented in Tables 6 to 9, respectively, and the corresponding tie line diagrams are shown as Figure 5 to 8. The sloping of tie lines to the ethyl acetate vertex in Figures 5 and 6 is very clear.

Table 5. Solubility Data for $[C_2OHdmim]BF_4$ (1) + Ethanol (2) + Ethyl Acetate (3) at T = 298.15 K

x_1	x_2	x_3	$\rho/g \cdot cm^{-3}$
0.700	0.000	0.300	1.070
0.547	0.160	0.294	1.046
0.475	0.228	0.297	1.037
0.402	0.299	0.299	1.030
0.351	0.349	0.300	1.016
0.306	0.386	0.308	1.005
0.247	0.437	0.317	0.998
0.204	0.469	0.327	0.976
0.161	0.501	0.338	0.958
0.136	0.514	0.350	0.938
0.110	0.521	0.369	0.908
0.088	0.527	0.385	0.882
0.075	0.524	0.402	0.874
0.065	0.513	0.423	0.868
0.053	0.514	0.433	0.865
0.040	0.495	0.465	0.862
0.030	0.477	0.493	0.860
0.023	0.455	0.522	0.869
0.017	0.433	0.550	0.862
0.013	0.401	0.587	0.859
0.009	0.373	0.618	0.858
0.007	0.345	0.648	0.855
0.006	0.312	0.682	0.852
0.005	0.270	0.725	0.848
0.005	0.231	0.764	0.845
0.005	0.204	0.791	0.841
0.004	0.175	0.821	0.837
0.004	0.130	0.866	0.831
0.002	0.100	0.898	0.825
0.002	0.060	0.939	0.817

On the basis of the four figures above, the four ionic liquids $[emim]BF_4$, $[C_2OHmim]BF_4$, $[edmim]BF_4$, and $[C_2OHdmim]BF_4$ can be used for ethyl acetate and ethanol separation by solvent extraction. The addition of a 25 % mole fraction $[emim]BF_4$ or $[C_2OHmim]BF_4$ or $[edmim]BF_4$ or $[C_2OHdmim]BF_4$ to a preconcentrated binary ethyl acetate + ethanol solution (such as 32 % mole fraction of ethyl acetate) causes a phase split. For $[emim]BF_4$, the upper phase contains about 70.5 % mole fraction of ethyl acetate, 25.3 % mole fraction of ethanol, and 4.2 % mole fraction of $[emim]BF_4$, and the lower phase consists of 43.5 % mole fraction of ethyl acetate, 26.5 % mole fraction of ethanol, and 30.0 % mole fraction of $[emim]BF_4$. In the upper phase, the ethyl acetate−ethanol preliminary composition has been changed.

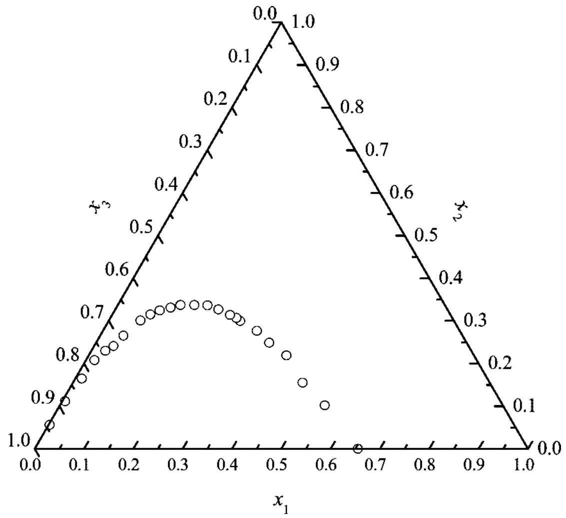

Figure 1. Solubility curve for $[emim]BF_4$ (1) + ethanol (2) + ethyl acetate (3) at T = 298.15 K.

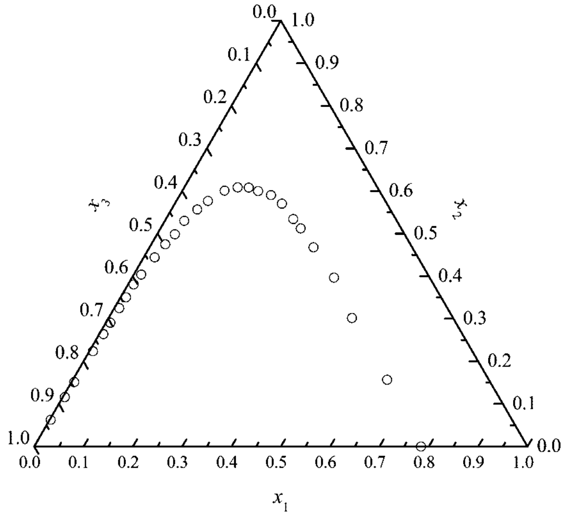

Figure 2. Solubility curve for [C_2OHmim]BF_4 (1) + ethanol (2) + ethyl acetate (3) at T = 298.15 K.

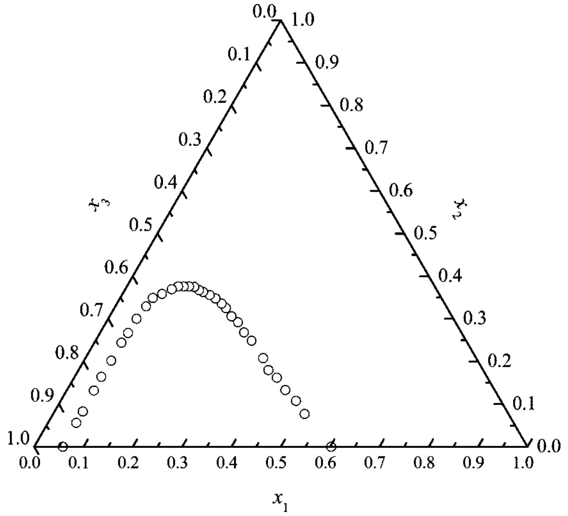

Figure 3. Solubility curve for [edmim]BF_4 (1) + ethanol (2) + ethyl acetate (3) at T = 298.15 K.

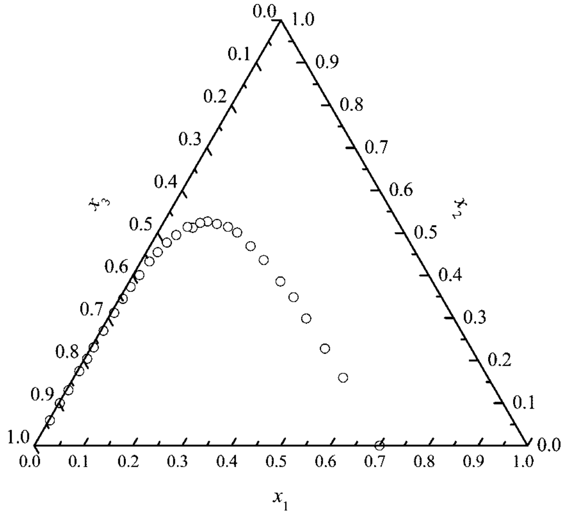

Figure 4. Solubility curve for [C_2OHdmim]BF_4 (1) + ethanol (2) + ethyl acetate (3) at T = 298.15 K.

Similarly for the other three ionic liquids, the ethyl acetate−ethanol mixture all divided into the ethyl acetate rich phase and the ionic liquid rich phase, which result in the distribution of ethanol in the two new phases.

Table 6. Tie Line Data for [emim]BF_4 (1) + Ethanol (2) + Ethyl Acetate (3) at T = 298.15 K

EA-rich phase			IL-rich phase				
x_1	x_2	x_3	x_1	x_2	x_3	β	S
0.004	0.077	0.919	0.621	0.042	0.337	0.546	1.490
0.005	0.096	0.898	0.608	0.056	0.335	0.584	1.563
0.007	0.117	0.876	0.557	0.085	0.359	0.722	1.763
0.009	0.137	0.853	0.472	0.137	0.391	0.996	2.170
0.012	0.158	0.831	0.406	0.177	0.417	1.123	2.238
0.016	0.201	0.783	0.360	0.216	0.424	1.075	1.985
0.029	0.226	0.745	0.329	0.240	0.431	1.062	1.836
0.054	0.280	0.666	0.269	0.293	0.438	1.045	1.588
0.071	0.303	0.627	0.236	0.315	0.449	1.040	1.452

Table 7. Tie Line Data for [C_2OHmim]BF_4 (1) + Ethanol (2) + Ethyl Acetate (3) at T = 298.15 K

EA-rich phase			IL-rich phase				
x_1	x_2	x_3	x_1	x_2	x_3	β	S
0.003	0.063	0.933	0.781	0.032	0.187	0.503	2.505
0.004	0.138	0.858	0.695	0.092	0.213	0.668	2.698
0.005	0.197	0.797	0.575	0.184	0.241	0.934	3.090
0.008	0.264	0.728	0.468	0.291	0.242	1.101	3.314
0.009	0.309	0.682	0.372	0.368	0.260	1.191	3.122
0.011	0.353	0.637	0.318	0.428	0.255	1.212	3.029
0.016	0.408	0.576	0.267	0.482	0.252	1.180	2.698
0.025	0.451	0.524	0.209	0.520	0.272	1.152	2.222

Table 8. Tie Line Data for [edmim]BF_4 (1) + Ethanol (2) + Ethyl Acetate (3) at T = 298.15 K

EA-rich phase			IL-rich phase				
x_1	x_2	x_3	x_1	x_2	x_3	β	S
0.057	0.062	0.881	0.564	0.037	0.399	0.597	1.317
0.058	0.104	0.838	0.506	0.080	0.414	0.762	1.540
0.058	0.147	0.795	0.459	0.138	0.403	0.940	1.853
0.058	0.203	0.739	0.420	0.177	0.403	0.873	1.603
0.059	0.252	0.689	0.381	0.218	0.401	0.863	1.481
0.063	0.303	0.634	0.334	0.263	0.403	0.868	1.364
0.070	0.336	0.594	0.286	0.306	0.409	0.909	1.320
0.080	0.350	0.569	0.244	0.334	0.422	0.953	1.285

Table 9. Tie Line Data for [C_2OHdmim]BF_4 (1) + Ethanol (2) + Ethyl Acetate (3) at T = 298.15 K

EA-rich phase			IL-rich phase				
x_1	x_2	x_3	x_1	x_2	x_3	β	S
0.003	0.126	0.871	0.616	0.084	0.301	0.664	1.926
0.004	0.163	0.833	0.520	0.153	0.327	0.939	2.390
0.006	0.238	0.756	0.428	0.238	0.335	0.999	2.259
0.008	0.285	0.707	0.357	0.290	0.352	1.019	2.046
0.012	0.341	0.647	0.310	0.346	0.345	1.014	1.903
0.018	0.392	0.590	0.260	0.423	0.317	1.079	2.006
0.019	0.433	0.548	0.212	0.437	0.351	1.008	1.574
0.022	0.445	0.533	0.165	0.453	0.382	1.018	1.420

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 ethanol + ethyl acetate mixture studied, the selectivity (S) of extracting ethanol from the mixture and the distribution ratio (β) of ethanol in two phases are given in terms of mole fraction as:

$$S = \frac{(x_2/x_3)\text{ ionic liquid rich phase}}{(x_2/x_3)\text{ ethyl acetate rich phase}}$$

$$\beta = \frac{(x_2)\text{ ionic liquid rich phase}}{(x_2)\text{ ethyl acetate rich phase}}$$

As Figure 9 shows, the relationship between the distribution ratio and the ethanol content in the ethyl acetate rich phase of the four ionic liquids is complicated and intercrossed at different districts of ethanol content. When the ethanol content in the

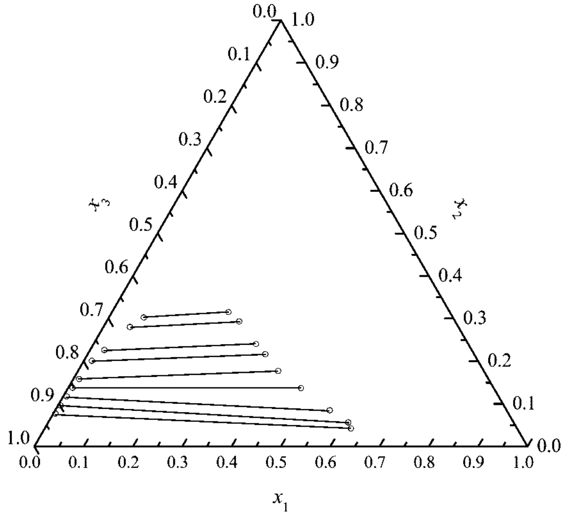

Figure 5. Tie lines for [emim]BF_4 (1) + ethanol (2) + ethyl acetate (3) at $T = 298.15$ K.

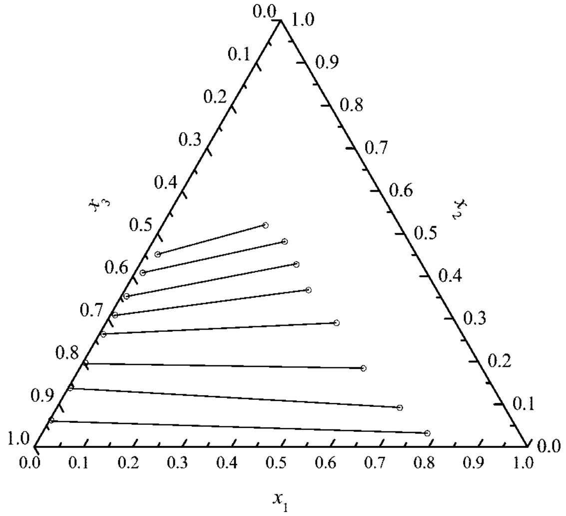

Figure 6. Tie lines for [C_2OHmim]BF_4 (1) + ethanol (2) + ethyl acetate (3) at $T = 298.15$ K.

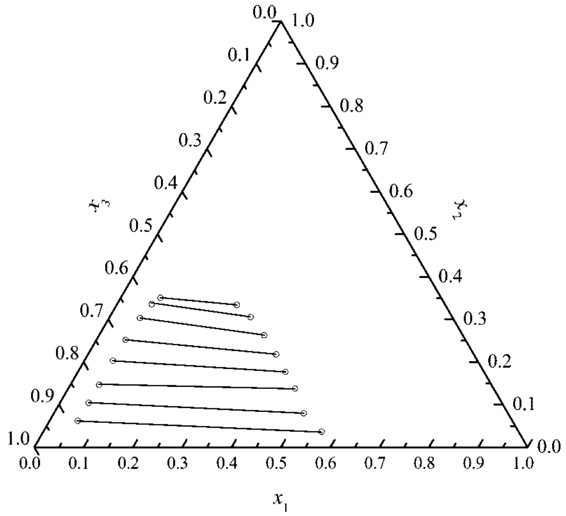

Figure 7. Tie lines for [edmim]BF_4 (1) + ethanol (2) + ethyl acetate (3) at $T = 298.15$ K.

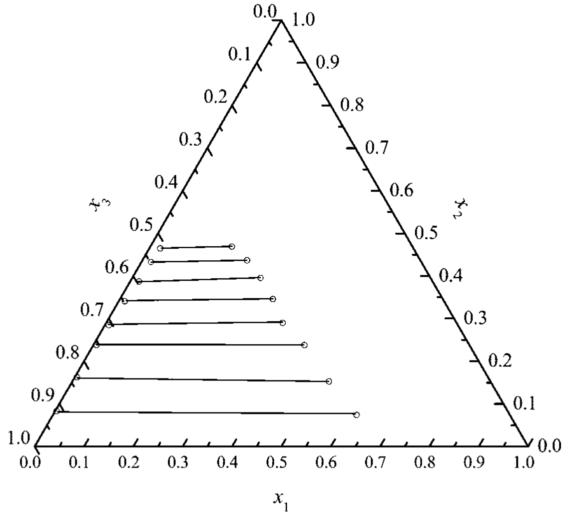

Figure 8. Tie lines for [C_2OHdmim]BF_4 (1) + ethanol (2) + ethyl acetate (3) at $T = 298.15$ K.

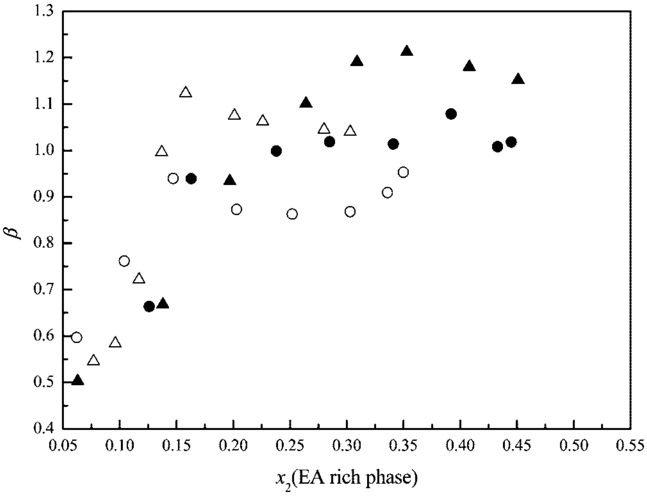

Figure 9. Comparison of distribution ratio. ▲, [C_2OHmim]BF_4; ●, [C_2OHdmim]BF_4; △, [emim]BF_4; ○, [edmim]BF_4. x_2 refers to the mole fraction of ethanol.

ethyl acetate rich phase arrives at about 0.13 mole fraction, the distribution ratio's order was [emim]BF_4 > [edmim]BF_4 > [C_2OHdmim]BF_4 > [C_2OHmim]BF_4, whereas when the ethanol content was about 0.3 mole fraction, the order changed into [C_2OHmim]BF_4 > [emim]BF_4 > [C_2OHdmim]BF_4 > [edmim]BF_4.

As Figure 10 shows, the selectivity of the four ionic liquids is alike. When the ethanol content in the ethyl acetate rich phase rises, the selectivity of ionic liquids goes up and then decreases. When the ethanol content in the ethyl acetate rich phase arrives at about 0.25 mole fraction, the selectivity of [C_2OHmim]BF_4 reaches the maximum, while the ethanol content is about 0.15 mole fraction for [emim]BF_4, [edmim]BF_4, and [C_2OHdmim]-BF_4. The order of the selectivity is [C_2OHmim]BF_4 > [C_2OHdmim]BF_4 > [emim]BF_4 > [edmim]BF_4. In the four ionic liquids studied, [edmim]BF_4 had an overall β less than 1.0, which means more ethanol was restrained in the EA phase than extracted into the IL phase. This may be a handicap in the separation of ethanol and ethyl acetate.

The selectivity of [emim]BF_4 is clearly larger than [edmim]BF_4, and the selectivity of [C_2OHmim]BF_4 is clearly large than [C_2OHdmim]BF_4. The difference between the selectivity values may results from [C_2OHdmim]BF_4 and [edmim]BF_4 having a C_2 position CH_3 instead of a 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

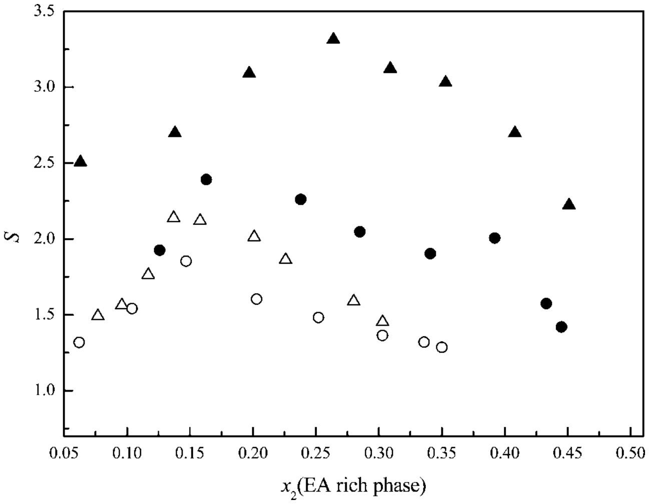

Figure 10. Comparison of selectivity. ▲, $[C_2OHmim]BF_4$; ●, $[C_2OHdmim]BF_4$; △, $[emim]BF_4$; ○, $[edmim]BF_4$. x_2 refers to the mole fraction of ethanol.

Table 10. Values of Parameters for the NRTL Equation for the Ternary Mixtures { $[emim]BF_4$ (1) or $[C_2OHmim]BF_4$ (1) or $[edmim]BF_4$ (1) or $[C_2OHdmim]BF_4$ (1) + Ethanol (2) + Ethyl Acetate (3)}

component (*i-j*)	τ_{ij}		α	rmsd
$[emim]BF_4$ (1), Ethanol (2), Ethyl Acetate (3)				
1–2	6.799	2.509	0.20	0.001
1–3	−2.327	10.390		
2–3	−1.891	3.952		
$[C_2OHmim]BF_4$ (1), Ethanol (2), Ethyl Acetate (3)				
1–2	9.041	3.262	0.20	0.008
1–3	−1.438	7.829		
2–3	−1.894	3.956		
$[edmim]BF_4$ (1), Ethanol (2), Ethyl Acetate (3)				
1–2	1.326	2.218	0.20	0.001
1–3	−1.138	4.947		
2–3	−1.893	3.954		
$[C_2OHdmim]BF_4$ (1), Ethanol (2), Ethyl Acetate (3)				
1–2	7.881	3.174	0.20	0.001
1–3	−1.982	9.749		
2–3	−1.895	3.955		

can presumably form a hydrogen bond with the alcohol at this hydrogen.[16] By replacing the hydrogen of the [emim] or $[C_2OHmim]$ cation with a methyl group (forming [edmim] or $[C_2OHdmim]$), the ability of the cation to form a hydrogen bond with ethanol is diminished, indirectly resulting in an increase in the mutual solubility of the ionic liquid $[edmim]BF_4$ or $[C_2OHdmim]BF_4$ and ethyl acetate, which explains why $[emim]BF_4$ has better extraction capacity than $[edmim]BF_4$ and $[C_2OHmim]BF_4$ is better than $[C_2OHdmim]BF_4$.

The selectivity of $[C_2OHmim]BF_4$ is clearly larger than $[emim]BF_4$, and the selectivity of $[C_2OHdmim]BF_4$ is clearly larger than $[edmim]BF_4$. The difference between the selectivity values may result from $[C_2OHmim]BF_4$ and $[C_2OHdmim]BF_4$ having a hydroxyl group. The hydroxyl group obviously enhances the interaction between the ionic liquid and ethanol. The order of the selectivity in the four ionic liquids shows that the hydroxyl group should have a stronger ability to affect the interaction between the ionic liquid and ethanol than the C_2 position H.

On the basis of the discussion above, $[C_2OHmim]BF_4$ has better extraction capacity than other studied ionic liquids, which can be the potential solvent for the separation of ester acetic and ethanol by liquid–liquid extraction. Compared with using VOCs, the use of ionic liquids to separate ethyl acetate and ethanol takes advantage of their low vapor pressure and their ability to be easily transported and reused.

Ionic liquids have been regarded as "designed" solvents by a combination of different anions and cations. We believe that this art of controlling the mutual solubility between ionic liquids and other solvents by adjusting groups at different positions of the cation should regarded as "further design" of ionic liquids.

Tie Line Correlation. The nonrandom two-liquid equation (NRTL) by Renon and Prausnitz[17] 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.[18–23]

In the conjugated solutions:

$$\chi_i\gamma_i = \chi^*_i\gamma^*_i$$

The objective function (OF) is defined as shown:

$$\mathrm{OF} = \ln(x_i^*/x_i) = \ln\gamma_i - \ln\gamma_i^*$$

where x_i = the mole fraction of the EA-rich phase; x_i^* = the mole fraction of the IL-rich phase; γ_i = the activity coefficient of the EA-rich phase; γ_i^* = the activity coefficient of the IL-rich phase; and i = the component indices.

The experimental values of OF were acquired by $\ln(x_i^*/x_i)$, while the calculated values of OF were obtained by $\ln\gamma_i - \ln\gamma_i^*$ through the NRTL equation.

The α (the nonrandomness parameter) value of 0.2 is commonly used.[24] τ (the interaction parameters) calculated values are not very different for $[C_2OHmim]BF_4$ and $[C_2OHdmim]BF_4$ because the two ionic liquids have a similar structure and physical properties. The only slight difference between the interaction parameter values may results from $[C_2OHdmim]BF_4$ having a C_2 position CH_3 instead of a C_2 position H as discussed above.

The interaction parameters τ calculated are quite different for $[C_2OHmim]BF_4$ and $[emim]BF_4$, and $[C_2OHmim]BF_4$ has better extraction capacity than $[emim]BF_4$ because the hydroxyl group has the strong ability to form a hydrogen bond with ethanol as discussed above.

The τ_{23} and τ_{32} calculated by the NRTL equation approach Arce's results,[24] which means these values are credible. The rmsd values from Table 10 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 NRTL model was obtained.

Conclusions

Liquid–liquid equilibrium data were obtained for the ternary mixtures of $[emim]BF_4$ or $[C_2OHmim]BF_4$ or $[edmim]BF_4$ or $[C_2OHdmim]BF_4$ + ethanol + ethyl acetate at 298.15 K. The extraction efficiencies of the four ionic liquids for the ethyl acetate + ethanol mixture were examined. The distribution ratio and selectivity values show that the hydroxyl group on cation can obviously enhance the interaction between the ionic liquid and ethanol, while the CH_3 group at the 2-*position* weakens these interactions. $[C_2OHmim]BF_4$ has better extraction capacity than the other studied ionic liquids, which can be the potential solvent for the separation of ester acetic and ethanol by liquid–liquid extraction.

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Received for review September 07, 2007. Accepted November 26, 2007. We would like to thank the financial support from the National Natural Science Foundation of China (Grant No. 20490209 and 20625621).

JE700516T