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A Promising Ionic Liquid [BMIM][FeCl$_4$] for the Extractive Separation of Aromatic and Aliphatic Hydrocarbons

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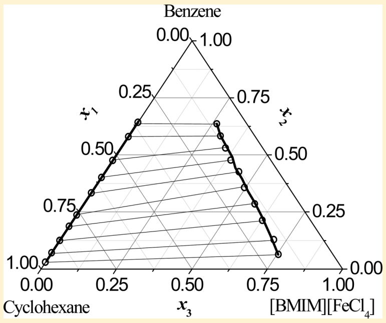
ABSTRACT: Liquid−liquid equilibria (LLE) of the following ternary systems were measured at atmospheric pressure, that is, {cyclohexane + benzene + [BMIM][FeCl$_4$]} at T = 298.15 K and 313.15 K, {n-hexane + benzene + [BMIM][FeCl$_4$]}, {n-heptane + toluene + [BMIM][FeCl$_4$]} at T = 298.15 K, and {cyclohexane + benzene + [BMIM]Cl} at T = 339.15 K. The extraction performance of ionic liquid (IL) [BMIM][FeCl$_4$] for the aromatic hydrocarbons (benzene or toluene) from their aliphatic hydrocarbons (cyclohexane, n-heptane, or n-hexane) was analyzed and compared with some imidazolium-based ILs. The results indicate that the IL [BMIM][FeCl$_4$] shows both higher extractive selectivity and distribution factor for the systems studied herein and thus is a promising solvent for the extractive separation of aromatic and aliphatic hydrocarbons. The LLE data were well-correlated by the nonrandom two-liquid (NRTL) model of nonelectrolyte solutions with the overall average absolute relative deviation (rmsd) being about 0.0188 in terms of the mole fraction based activity.



INTRODUCTION

Separation of aromatic and aliphatic mixtures via conventional distillation is a costly process due to their close volatility and even the presence of azeotropism, and thus their separation is practically achieved through liquid extraction[1] for the aromatic content in the range of (20 to 65) wt % with some specific solvents, for example, sulfolane,[2−5] N-methyl pyrrolidone (NMP),[4] ethylene glycols,[5−7] and propylene carbonate[8] and so forth, or through azeotropic distillation or extractive distillation depending on the content of aromatics in the stream. However, these organic extracting solvents are generally toxic, volatile, flammable, and hard to be recycled facilely due to their mutual solubility with the naphtha to be separated. To overcome these demerits, ionic liquids (ILs) as novel and greener solvents have attracted much attention in recent years[9−11] due to their unique characteristics and sharp contrast to the molecular solvents, for example, less toxicity, nonvolatility, nonflammability, and negligible solubility in hydrocarbon mixtures and thus easier to be recycled. Meanwhile, the number of ILs is so huge that a satisfactory extractant can be always expected or designed through appropriate combination of cation and anion. Until now, many experimental data of liquid−liquid equilibria (LLE) have been reported for the (IL + aromatic + aliphatic) systems with varying ILs,[12−22] where the cations are mostly alkyl (R-) substituted imidazolium or pyridinium, while the anions are diversified including halide, PF$_6$, BF$_4$, dialkyl-phosphate, alkyl-sulfate, and bis-{(trifluoromethyl)sulfonyl}amide, and so forth. These results are helpful for screening a promising IL for the extractive separation of an aromatic−aliphatic mixture, as well as for a better insight into the relationship between the extraction performance and the structure of ILs, which in return can guide the molecular design of task-specific ILs. In effect, some preliminary conclusions have been achieved. First, the preferential extractability of ILs for the aromatic components is mainly arisen from the $\pi-\pi$ interaction between the aromatic cation of ILs, that is, imidazolium or pyridinium, and the aromatic molecules.[23] Second, the length of the alkyl substitute to the imidazolium or pyridinium cation is vital to tuning the physicochemical properties of ILs, for example, the solubility of ILs for different hydrocarbons and thus their extractive selectivity and capacity for the aromatic component. Third, the anion of the ILs might be a secondary factor in comparison with cation, although it has a deterministic role on the hydrophobicity of the ILs. For example, ILs [BMIM]PF$_6$ and [BMIM]BF$_4$ show a comparable extraction ability for benzene from its cyclohexane mixture at ambient temperatures, but their hydrophobicity is totally different, being hydrophobic and hydrophilic ILs, respectively. Finally, an IL with a high selectivity for the aromatic component is always accompanied with a lower capacity and vice versa.

Based on the above cognition, a candidate IL for the separation of aromatic/aliphatic mixture is better composed of an aromatic cation, for example, R-substituted imidazolium or pyridinium, and an appropriate anion that makes the ILs suitable for practical use. More specifically, the ILs should have a good extracting ability for aromatic component along with high stability, low viscosity and toxicity, and ease of preparation

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and low cost. In this regard, the feasibility of ILs 1-butyl-3-methylimidazolium chloride [BMIM]Cl[24] and [BMIM]-$[FeCl_4]$[25,26] is worthy of study. Besides, the LLE data for the present ILs with aromatic (benzene, toluene) and aliphatic (cyclohexane, *n*-hexane, *n*-heptane) binary mixtures are not available. Therefore, the LLE data for the following ternary systems at atmospheric pressure and different temperatures were measured, namely, {cyclohexane + benzene + [BMIM]$[FeCl_4]$}, {*n*-hexane + benzene + [BMIM]$[FeCl_4]$}, {*n*-heptane + toluene + [BMIM]$[FeCl_4]$}, and {cyclohexane + benzene + [BMIM][Cl]}, and the experimental data were correlated by the nonrandom two-liquid (NRTL) model.

EXPERIMENTAL SECTION

Materials. The chemicals used in this study were all purchased from Beijing Chemical Reagent Factory, of which benzene, cyclohexane, *n*-hexane, toluene, and *n*-heptane are with a nominal minimum mass fraction of 0.995. *N*-Methylimidazole, chlorobutane, diethyl ether, and ethanol anhydrous are of analytical reagent (AR) grade reagents and were used as received.

Preparation of ILs [BMIM]Cl and [BMIM]$[FeCl_4]$. [BMIM]Cl was synthesized by refluxing the mixture of *N*-methylimidazole and chlorobutane at 90 °C for 12 h with ca. 10 % excess stoichiometric chlorobutane. The excessive reactants of the raw product were removed first by rotary evaporation under reduced pressure and then washed three times with equal volume of diethyl ether. The resulting white precipitate, that is, [BMIM]Cl at room temperature, was filtrated and dried in a vacuum oven. The melting point of [BMIM][Cl] is measured by DSC being approximately 60.3 °C. The water content of [BMIM][Cl] is analyzed by Karl Fischer method as 1415 ppm. The purity of [BMIM][Cl] is confirmed qualitatively from both ^{1}H NMR and ^{13}C NMR spectra, and its purity is estimated being about 0.986 in mole fraction. [BMIM]$[FeCl_4]$ was prepared by mixing equal moles of anhydrous iron chloride dissolved in ethanol anhydrous and [BMIM]Cl. The mixture was left stirring overnight at room temperature and then treated by a rotary evaporator to remove ethanol and other residual volatile impurities, and the water mass fraction was less than $4 \cdot 10^{-4}$ as measured by the Karl Fischer titrator (CBS-1A). The purity of the final IL [BMIM]$[FeCl_4]$ is above 0.99 in mole fraction in terms of its elementary analysis results and ^{1}H NMR analysis for its precursor [BMIM]Cl.

Apparatus and Procedures. The LLE measurements were conducted in a jacketed glass cell of about 150 mL sealed by a silicon rubber cap. The equilibrium liquid temperature was maintained by circulating water coming from a super thermostat with temperature fluctuation within (± 0.1 °C). First, known masses of ILs and liquid mixtures with known composition were in turn added into the glass cell. The mixture was stirred with a magnetic stirrer for at least 1.5 h at specified temperature and then stopped stirring for 2 h to achieve a clear phase separation. The time used here for equilibrium and phase splitting was justified by some preliminary tests. Two samples (about 1.0 mL for each) were taken out from both phases, added immediately into two 10 mL test tubes, and weighed their exact masses. Each tube was prefilled with about 3 mL of internal standard and 3 mL of water with their exact masses known in advance for the sake of mass balance. The tubes were sealed with PTFE/silicone sheet, shaken for 10 min, and then put aside overnight for settling. In this process, the organic mixture, namely, {benzene + cyclohexane}, {benzene + *n*-hexane}, or {toluene + *n*-heptane}, is transferred into the upper organic phase, while the IL component into the bottom water phase completely. Samples from the organic phase are totally free of IL, which is adopted by many authors and justified by relevant analysis techniques.[27,28]

The relative composition of the binary mixtures, that is, (benzene and cyclohexane), (benzene and *n*-hexane), and (toluene and *n*-heptane), in the pretreated samples was analyzed using gas chromatography (Shimadzu GC2010 equipped with a FID detector and FFAP capillary column, 30 m × 0.25 mm i.d. × 5 μm; carrier gas N_2; temperature program: (70 to 170) °C at 10 $°C \cdot min^{-1}$ and then maintained at 170 °C for 30 min. The sample concentration was given by the GC solution workstation according to the area of each chromatograph peak and the calibration curve made prior for the ternary mixtures of (toluene + benzene + cyclohexane), (toluene + benzene + *n*-hexane), (benzene + toluene + *n*-heptane). Once the amount of each component for the binary system, namely, (benzene and cyclohexane), (benzene and *n*-hexane), or (toluene and *n*-heptane), had been determined, the mass fraction of IL in corresponding both phases was calculated via mass balance for the upper and bottom phase samples, respectively. At least two samples were made for each phase, and three injections were made for each sample in the GC analysis. The reproducibility of the composition is within ± 1 %. The uncertainty of mole fraction for cyclohexane, benzene, *n*-hexane, toluene, and *n*-heptane is ± 0.005 and for ILs is within ± 0.002 as estimated from the water content of the IL used. All components were prepared gravimetrically by an electronic balance (type AR2130, Ohaus Corp., USA) with a readability of 0.001 g.

RESULTS AND DISCUSSION

The experimental LLE data for the four ternary systems, namely, {cyclohexane (1) + benzene (2) + [BMIM]$[FeCl_4]$ (3)}, {*n*-hexane (1) + benzene (2) + [BMIM]$[FeCl_4]$ (3)}, {*n*-heptane (1) + toluene (2) + [BMIM]$[FeCl_4]$ (3)}, and {cyclohexane + benzene + [BMIM][Cl]}, at different temperatures are presented in Tables 1 to 4, respectively. The resulting phase diagrams for the first three systems above at 298.15 K and for the last system at 339.15 K are shown in Figures 1 to 4, respectively. As seen from Figures 1 to 4, the liquid composition of the IL phase varies regularly with that of the organic raffinate phase, and the data distribution in the figures follows a definite pattern with low scattering, which justifies the experimental method used herein and lays a foundation for the data correlation with an appropriate thermodynamic model. Further, the binodal curves for the ternary systems with IL [BMIM]$[FeCl_4]$, that is, Figures 1 to 3, are more symmetrical than that with IL [BMIM]Cl, implying that [BMIM]$[FeCl_4]$ has a higher extracting capacity for the aromatic components than [BMIM]Cl.

The selectivity (*S*) and distribution ratio (*D*) of the aromatic component are two important parameters in assessing the feasibility of an IL for the extractive separation of aromatics, and thus they are also listed in Tables 1 to 4. The values of *S* and *D* were calculated by virtue of the experimental LLE data using eqs 1 and 2 below.

$$S = \frac{(x_2''/x_1'')}{(x_2'/x_1')} \tag{1}$$

Table 1. LLE Data in Mole Fraction for the {Cyclohexane (1) + Benzene (2) + [BMIM][FeCl$_4$] (3)} System at Pressure p = 0.1 MPa and 298.15 K and 313.15 K along with the Selectivity (S) and Distribution Factor of Benzene (D)[a]

organic phase		IL phase			
x'_1	x'_2	x''_1	x''_2	S	D
		T = 298.15 K			
0.970	0.030	0.181	0.064	11.55	2.16
0.929	0.071	0.164	0.128	10.14	1.79
0.875	0.125	0.160	0.213	9.34	1.70
0.813	0.187	0.149	0.285	8.31	1.52
0.763	0.237	0.147	0.357	7.80	1.51
0.666	0.334	0.131	0.426	6.51	1.28
0.599	0.401	0.132	0.477	5.38	1.19
0.524	0.476	0.123	0.530	4.73	1.11
0.420	0.580	0.113	0.583	3.73	1.01
0.357	0.643	0.099	0.636	3.58	0.99
		T = 313.15 K			
0.968	0.032	0.194	0.058	9.19	1.84
0.938	0.062	0.207	0.112	8.15	1.80
0.879	0.121	0.179	0.201	8.16	1.66
0.816	0.184	0.174	0.282	7.19	1.53
0.749	0.251	0.183	0.342	5.56	1.36
0.670	0.330	0.153	0.409	5.45	1.24
0.588	0.412	0.139	0.467	4.79	1.13
0.501	0.499	0.129	0.520	4.07	1.04
0.390	0.610	0.117	0.577	3.15	0.94
0.282	0.718	0.095	0.645	2.68	0.90

[a] The standard uncertainty u is $u(T)$ = 0.3 K, and the combined standard uncertainty u_c is $u_c(x)$ = 0.0013.

Table 2. LLE Data in Mole Fraction for the {n-Hexane (1) + Benzene (2) + [BMIM][FeCl$_4$] (3)} System at Pressure p = 0.1 MPa and 298.15 K along with the Selectivity (S) and Distribution Factor of Benzene (D)[a]

organic phase		IL phase			
x'_1	x'_2	x''_1	x''_2	S	D
0.966	0.034	0.165	0.078	13.26	2.27
0.939	0.061	0.160	0.125	12.00	2.04
0.881	0.119	0.138	0.215	11.62	1.81
0.810	0.190	0.113	0.323	12.16	1.70
0.746	0.254	0.099	0.376	11.15	1.48
0.676	0.324	0.091	0.456	10.42	1.40
0.614	0.386	0.088	0.505	9.18	1.31
0.518	0.482	0.085	0.553	6.97	1.15
0.423	0.577	0.079	0.593	5.50	1.03
0.315	0.685	0.070	0.673	4.43	0.98

[a] The standard uncertainty u is $u(T)$ = 0.3 K, and the combined standard uncertainty u_c is $u_c(x)$ = 0.0012.

$$D = \frac{(x''_2)}{(x'_2)} \tag{2}$$

where x_1 and x_2 refer to the mole fraction of aliphatic and aromatic, respectively, ′ represents the organic phase, and ″ represents the IL phase.

To compare the selectivity of different ILs for the aromatic components from their aliphatic mixtures at varying conditions, the selectivity for the four ternary systems studied here is presented in Figure 5. By analyzing this figure, some conclusions can be drawn. First, the selectivity values for all of the systems studied are higher than unity except one point for the {cyclohexane + benzene + [BMIM]Cl} system at a mole fraction of benzene above 0.8. This indicates that both ILs [BMIM][FeCl$_4$] and [BMIM]Cl show a preferential extracting ability for the aromatic components from their corresponding aliphatic binary mixtures, which may be ascribed to the specific π−π electron interaction between benzyl ring and the aromatic

Table 3. LLE Data in Mole Fraction for the {n-Heptane (1) + Toluene (2) + [BMIM][FeCl$_4$] (3)} System at Pressure p = 0.1 MPa and 298.15 K along with the Selectivity (S) and Distribution Factor of Toluene (D)[a]

organic phase		IL phase			
x'_1	x'_2	x''_1	x''_2	S	D
0.950	0.050	0.159	0.089	10.69	1.79
0.920	0.080	0.175	0.126	8.17	1.56
0.856	0.144	0.170	0.194	6.76	1.35
0.784	0.216	0.165	0.248	5.43	1.14
0.710	0.290	0.158	0.305	4.71	1.05
0.634	0.366	0.152	0.361	4.11	0.99
0.567	0.433	0.144	0.406	3.67	0.94
0.478	0.522	0.139	0.454	2.99	0.87
0.389	0.611	0.133	0.499	2.39	0.82
0.262	0.738	0.120	0.568	1.67	0.77

[a] The standard uncertainty u is $u(T)$ = 0.3 K, and the combined standard uncertainty u_c is $u_c(x)$ = 0.0007.

Table 4. LLE Data in Mole Fraction for the {Cyclohexane (1) + Benzene (2) + [BMIM]Cl (3)} System at Pressure p = 0.1 MPa and 339.15 K along with the Selectivity (S) and Distribution Factor of Benzene (D)[a]

organic phase		IL phase			
x'_1	x'_2	x''_1	x''_2	S	D
0.935	0.065	0.091	0.025	4.04	0.39
0.888	0.112	0.085	0.043	4.03	0.38
0.812	0.188	0.083	0.073	3.82	0.39
0.722	0.278	0.081	0.109	3.51	0.39
0.634	0.366	0.075	0.141	3.25	0.38
0.540	0.460	0.076	0.179	2.77	0.39
0.445	0.555	0.069	0.211	2.44	0.38
0.346	0.654	0.065	0.242	1.98	0.37
0.250	0.750	0.063	0.284	1.51	0.38
0.143	0.857	0.059	0.326	0.93	0.38

[a] The standard uncertainty u is $u(T)$ = 0.3 K, and the combined standard uncertainty u_c is $u_c(x)$ = 0.0008.

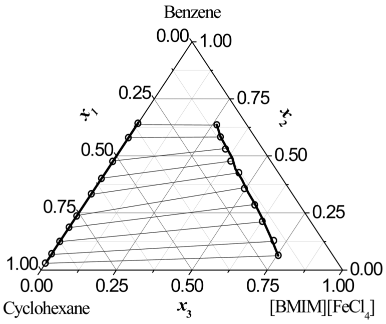

Figure 1. Binodal curves and tie lines for the ternary mixture {cyclohexane (1) + benzene (2) + [BMIM][FeCl$_4$] (3)} at 298.15 K. —, Predicted line by the NRTL equation; ○, experimental data.

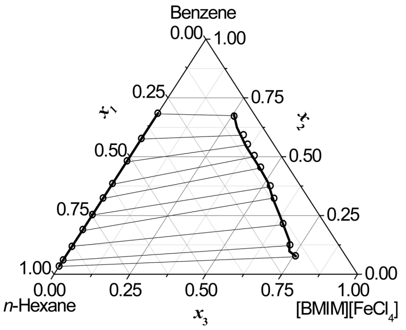

Figure 2. Binodal curves and tie-lines for the ternary mixture {*n*-hexane (1) + benzene (2) + [BMIM][FeCl$_4$] (3)} at 298.15 K. —, Predicted line by the NRTL equation; ○, experimental data.

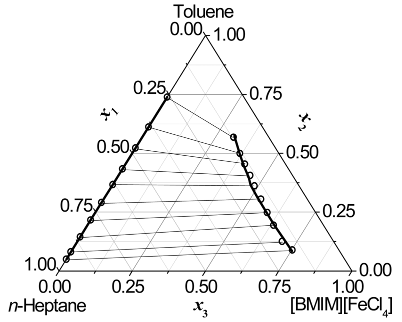

Figure 3. Binodal curves and tie-lines for the ternary mixture {*n*-heptane (1) + toluene (2) + [BMIM][FeCl$_4$] (3)} at 298.15 K. —, Predicted line by the NRTL equation; ○, experimental data.

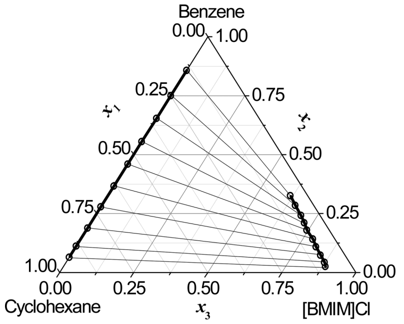

Figure 4. Binodal curves and tie-lines for the ternary mixture {cyclohexane (1) + benzene (2) + [BMIM]Cl (3)} at 339.15 K. —, Predicted line by the NRTL equation; ○, experimental data.

imidazolium cation irrespective of the anions involved in the ILs. Second, the effect of temperature on the selectivity of IL for the aromatic component is relatively weak, as indicated by the selectivity of [BMIM][FeCl$_4$] for benzene from its cyclohexane mixture at 298.15 K and 313.15 K, which may be attributed to the weak response of the $\pi-\pi$ electron interaction to the temperature.[11] Interestingly, a lower temperature favors a higher selectivity of the IL for the aromatic component, which is helpful for the practical use of IL in an aromatic extraction process. Therefore, LLE data measurements for other ternary systems were all conducted at 298.15 K unless stated otherwise. Third, the selectivity always decreases with the increase of the concentration of aromatic component in the raffinate for all of the systems studied, which is common for all aromatic extraction processes, and the maximum selectivity corresponds to the infinite dilution of the aromatic in its aliphatic mixture, being $\gamma^{\infty}_{2,\text{aliphatic}}/\gamma^{\infty}_{2,\text{IL}}$ as derived from eq 1. Fourth, the selectivity of IL [BMIM][FeCl$_4$] for the aromatic component from different binary mixtures at fixed other conditions follows the order (benzene + *n*-hexane) > (benzene + cyclohexane) > (toluene + *n*-heptane). This observation is consistent with the increasing similarity of the aromatic/aliphatic mixture in terms of their molecular structure and intermolecular interaction and thus may be universal for other ILs. Finally, the extraction selectivity of IL [BMIM][FeCl$_4$] is much higher than that of [BMIM]Cl for the cyclohexane-benzene mixture, which is solely originated from the influence of anion type. More specifically, the [FeCl$_4$] anion, as a complex of Cl$^-$ and Lewis acid FeCl$_3$, shows a stronger acidity than the chloride and thus introduces additional electron donor−acceptor interaction between IL and the benzyl ring, leading to a higher selectivity for the aromatic components. Moreover, [BMIM][FeCl$_4$] is a hydrophobic IL with much lower viscosity and melting temperature in comparison with [BMIM]Cl and thus advantageous as a promising candidate for the aromatic extraction process.

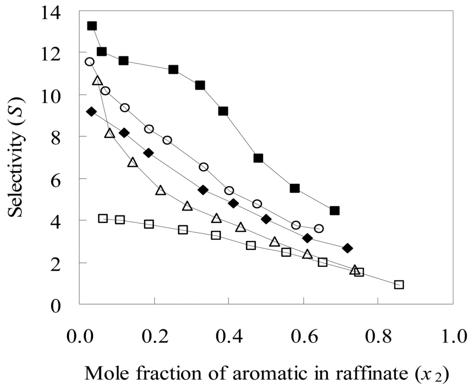

Figure 5. Selectivity of ILs for the aromatic component for ternary systems, as a function of the mole fraction of the aromatic in the raffinate. Mixtures: ○, ◆, {cyclohexane + benzene + [BMIM][FeCl$_4$]} at (298.15 and 313.15) K, respectively; ■, {*n*-hexane + benzene + [BMIM][FeCl$_4$]}, at 298.15 K; △, {*n*-heptane + toluene + [BMIM][FeCl$_4$]}, at 298.15 K; □, {cyclohexane + benzene + [BMIM]Cl} at 325.15 K.

The distribution factor of aromatic component between IL and the alkane phases for different ternary systems is presented in Figure 6. By comparing Figures 5 and 6, it is obvious that the variation extent of the distribution factor for all systems is much lower than that of the selectivity for the influencing factors studied, for example, temperature, and structural difference between aromatic and aliphatic components. Second, IL [BMIM][FeCl$_4$] shows a much higher extracting capacity than [BMIM]Cl since the distribution factor of the aromatic component between [BMIM][FeCl$_4$] and hydrocarbon is about two to five times higher than that between [BMIM]Cl and hydrocarbon. The higher extraction capacity of [BMIM][FeCl$_4$] coincides with the larger interionic interstice among large cations and anions in comparison with [BMIM]Cl, leading to a higher filling capacity for aromatic molecules. Third, the extracting capacity of [BMIM][FeCl$_4$] for different aromatic−aliphatic mixtures follows the order (benzene/*n*-hexane) > (benzene/cyclohexane) > (toluene/*n*-heptane), being same as the selectivity order, which may be closely related to the solubility of different pure components in [BMIM][FeCl$_4$]. To verify this assumption, the solubility of the pure component in [BMIM][FeCl$_4$] at 298.15 K was measured via a gravimetric method by weighing the mass difference of the

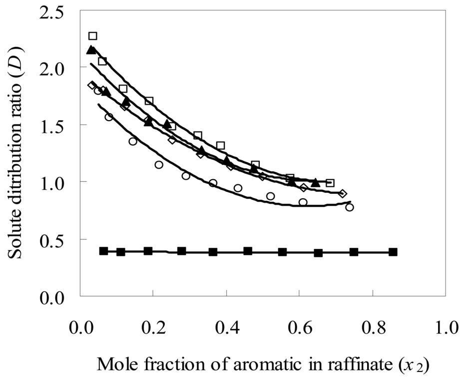

Figure 6. Distribution factor of aromatic component between IL and hydrocarbon raffinate for the ternary systems, as a function of the mole fraction of the aromatic in the raffinate phase. Mixtures: ▲, ◇, {cyclohexane + benzene + [BMIM][FeCl$_4$]} at (298.15 and 313.15) K, respectively; □, {n-hexane + benzene + [BMIM][FeCl$_4$]}, at 298.15 K; ○, {n-heptane + toluene + [BMIM][FeCl$_4$]}, at 298.15 K; ■, {cyclohexane + benzene + [BMIM]Cl} at 339.15 K.

Table 5. Maximum Distribution Factor and Selectivity of Different ILs for the Aromatic/Alkane Mixtures

ionic liquids	aromatic + alkane mixture	T/K	D_{aromatic}	S	ref
[BMIM][PF$_6$]	benzene/cyclohexane	295.15	0.66	3.1	30
[MMIM][DMP]	benzene/cyclohexane	298.15		3.6	15
[EMIM][DEP]	benzene/cyclohexane	298.15		3.7	15
[BMIM][FeCl$_4$]	benzene/cyclohexane	298.15	2.16	11.55	this work
[BMIM][FeCl$_4$]	benzene/n-hexane	298.15	2.27	13.26	this work
[BMIM][FeCl$_4$]	toluene/ n-heptane	298.15	1.79	10.69	this work
[BMIM]Cl	benzene/cyclohexane	339.15	0.39	4.04	this work
[OMIM]Cl	benzene/n-heptane	298.15	0.69	5.7	12
[OMIM]Cl	toluene/n-heptane	313.15	0.43	7.7	31
[BMIM][BF$_4$]	benzene/cyclohexane	323.15	0.56	15.9	32
[BMIM][BF$_4$]	toluene/n-heptane	323.15	0.42	29.5	33
sulfolane	benzene/n-hexane	303.15	0.35	29.1	36
sulfolane	toluene/n-heptane	313.15	0.31	33.0	36

solute saturated IL samples before and after vacuum vaporization. The solubility of benzene, toluene, cyclohexane, n-hexane, and n-heptane in mole fraction basis was determined as 0.795, 0.714, 0.451, 0.402, and 0.073, respectively. The solubility follows the order benzene > toluene > cyclohexane > n-hexane > n-heptane, indicating that aromatic compounds are more soluble in ILs than aliphatic compounds of a similar size,[23,29,30] and the lower solubility of alkyl benzene versus benzene may be related to its weaker interaction with the aromatic cation due to the steric hindrance of the alkyl substitute present and also its lower filling ability into the interstice of the IL phase.

By comparing the extraction performance of the two ILs, namely, [BMIM][FeCl$_4$] and [BMIM]Cl, for benzene from its cyclohexane mixture, as presented in Figures 5 and 6, it is obvious that [BMIM][FeCl$_4$] is much superior to [BMIM]Cl in terms of either selectivity or capacity. This conclusion may be applicable for other aromatic−aliphatic mixtures, since the stronger acidity and the larger size of the [FeCl$_4$] anion versus the Cl anion can result in a stronger interaction with aromatic ring and a larger interstice among cations and anions of the IL, and accordingly a higher extraction selectivity and capacity for the aromatic component. Moreover, in comparison with [BMIM]Cl, [BMIM][FeCl$_4$] is a hydrophobic room temperature ionic liquid with good fluidity and stability, ease of preparation, and insensitivity to water. To show the excellent performance of IL [BMIM][FeCl$_4$] for aromatic extraction, the selectivity and distribution factor values for several ILs reported until now were collected and compared in Table 5. It is shown that the imidazolium based ILs with [FeCl$_4$] anion show an excellent combination of both selectivity and distribution factor in comparison with other ILs,[15,12,30−33,36] for example, [BMIM][BF$_4$], and sulfolane has a little higher selectivity for aromatic component, but its extraction capacity is much lower than [BMIM][FeCl$_4$]. Further, the higher aromatic selectivity is only found for the ILs with [BF$_4$] and [FeCl$_4$] anions, which may be associated with their stronger Lewis acidity than the corresponding halide anions, that is, F and Cl, and other anions like [PF$_6$] and dialkylphosphates, for example, [DMP] and [DEP].

Tie-Line Correlation. For correlating the experimental LLE data of the ternary systems, the NRTL model of nonelectrolyte solutions developed by Renon and Prausnitz[34] was adopted for the calculation of activity coefficients at specified temperature and liquid compositions. This means that the ionic liquid component is treated herein as a neutral molecule instead of strong electrolyte dissociated completely, which is consistent with the weak dielectric property of aliphatic and aromatic hydrocarbons.

The experimental LLE data are fitted using the Levenberg−Marquardt (LM) algorithm via minimization of the following objective function (OF):

$$\text{OF} = \sum_{i}^{\text{NP}} [(x'_{1i}\gamma'_{1i} - x''_{1i}\gamma''_{1i})^2 + (x'_{2i}\gamma'_{2i} - x''_{2i}\gamma''_{2i})^2] \tag{3}$$

where NP is the number of data points, 1 and 2 are components 1 and 2 for a ternary system, respectively; the superscripts ′ and ″ refer to top and bottom phases in equilibrium, respectively; x and γ represent the mole fraction and activity coefficients, respectively. The accuracy of the correlation or prediction is represented in terms of the average absolute relative deviation (rmsd), given by eq 4

$$\text{rmsd} = \frac{1}{6\text{NP}}\sqrt{\sum_{i}^{m}\sum_{j}^{n-1}(x_{ij}^{\alpha}\gamma_{ij}^{\alpha} - x_{ij}^{\beta}\gamma_{ij}^{\beta})^2} \tag{4}$$

Here, m and n are the numbers of tie lines and components for a ternary system.

The regressed binary interaction parameters for the NRTL model are presented in Table 6. It should be pointed out that the pairwise interaction parameters for (aromatic + aliphatic) is taken from literature.[15,27,35]

Figures 1 to 4 showed the experimental LLE data for studied ternary systems {aliphatic (1) + aromatic (2) [BMIM][FeCl$_4$] (3)} compared with that predicted by the NRTL model. It is seen that the experimental data in the triangle phase diagram vary regularly with composition, and the calculated results go smoothly through the experimental data points. This along with the low correlation deviation in terms of an overall rmsd

Table 6. NRTL Binary Parameters Regressed from LLE Data and the Fitting Deviation in rmsd for Ternary Mixtures {Aliphatic (1) + Aromatic (2) + ILs (3)}

component	NRTL parameters			
		$(g_{ij} - g_{jj})$	$(g_{ji} - g_{ii})$	
(*i*) + (*j*)	α_{ij}	J·mol^{-1}	J·mol^{-1}	rmsd
cyclohexane (1) + benzene (2)[15]	0.45	5877.7	178.05	
		[BMIM][FeCl$_4$]		
cyclohexane (1) + IL (3)	0.1680	7906.897	837.375	0.011
benzene (2) + IL (3)	0.6047	18903.190	4968.146	
		[BMIM][Cl]		
cyclohexane (1) + IL (3)	0.338	8136.219	5594.513	0.045
benzene (2) + IL (3)	0.4528	10513.72	5693.221	
n-hexane (1) + benzene (2)[27]	0.4	6302.94	12211.66	
		[BMIM][FeCl$_4$]		
n-hexane (1) + IL (3)	0.2542	2237.019	5653.548	0.011
benzene (2) + IL (3)	0.4035	12870.150	4581.236	
n-heptane (1) + toluene (2)[35]	0.3001	1020.1	1143.8	
		[BMIM][FeCl$_4$]		
n-heptane (1) + IL (3)	0.3182	7386.702	3536.274	0.008
toluene (2) + IL (3)	0.3720	15147.42	−846.141	
	overall RMSD = 0.0188			

justified the applicability of the NRTL model for the representation of the LLE data for the IL-containing ternary systems studied here.

■ CONCLUSIONS

A promising ionic liquid [BMIM][FeCl$_4$] is found for the extractive separation of aromatic−aliphatic mixture for its both higher selectivity and capacity for the aromatic components studied, that is, benzene and toluene, along with its favorable attributes, for example, ease of preparation and cheapness, good fluidity, and stability. The extractive selectivity of [BMIM]-[FeCl$_4$] for all of the studied systems shows the order of (benzene/*n*-hexane) > (benzene/cyclohexane) > (toluene/*n*-heptane), being consistent with other ILs reported with the same cation but different anions. The higher extraction selectivity of [BMIM][FeCl$_4$] is ascribed to the additional interaction between acidic anion and the aromatic ring besides the $\pi-\pi$ interaction between aromatic cation and the aromatic solute, and the higher extracting capacity may be attributed to its larger interionic interstice and accordingly a higher filling capacity for aromatic molecules. The experimental LLE data can be well-correlated through the NRTL model for non-electrolyte solutions with an overall rmsd being about 0.0188.

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Notes

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