

## The Promising Ionic Liquids with Transition Metal Halide Anions for the Extractive Separation of Aromatic and Aliphatic Mixtures

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### Abstract

Ionic liquids (ILs) based on imidazolium and pyridinium cations and different types of anions contains transition metals were investigated for extraction of benzene from cyclohexane. The liquid-liquid equilibrium (LLE) data are presented for six ternary systems of (Cyclohexane + Benzene + an ionic Liquid) at 298.15K and atmospheric pressure. The ILs used in these systems are [Bmim][FeCl<sub>4</sub>], [Bmim][AlCl<sub>4</sub>], [BuPy][FeCl<sub>4</sub>], and [BuPy][AlCl<sub>4</sub>]. The influence cation and anion structure of ILs on the separation selectivity and capacity for aliphatic/aromatic mixtures was analyzed. The results indicate that most ILs investigated shows both higher extractive selectivity and capacity for the aromatic components for the systems studied herein, suggesting they can be used as promising extractants for the separation of aliphatic/aromatic mixtures. The LLE data were well correlated by the NRTL model of non-electrolyte solutions with overall ARD deviation being about 0.0001 in term of the mole fraction based activity.

*Keywords:* Liquid-liquid equilibria; ionic liquids; NRTL; aromatic compound; aliphatic compound.

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### 1. Introduction

The separation of aromatic from aliphatic compounds is of great importance for the petrochemical industry, especially when to meet the high demand of aromatic compounds by chemical industry, and the strict legal restrictions on the content of aromatics in gasoline. The aromatic hydrocarbons are separated from naphtha using a typical liquid-liquid extraction process [1]. Some conventional organic chemicals, such as sulfolane [2], N-formylmorpholine [3], Nmethylimidazole or N-ethylimidazole [4], glycols [5-7], propylene carbonate [8], or combinations of solvents, are used for the extraction of aromatics. However, these organic extracting solvents are generally toxic, volatile, flammable, and hard to be recycled facially due to their mutual solubility with the naphtha to be separated. In separations, a distillation step is usually also necessary to separate the solvent used from extract and raffinate phases. Nevertheless, when the ionic liq-

uids (ILs) are used, the process is much simpler because no distillation step is necessary, and the recovery of the ionic liquid solvent is much easier [9]. In recent years, ionic liquids have been reported as potentially good replacements for conventional solvents, due to their unique characteristics and sharp contrast to the molecular solvents, e.g. less toxicity, non-volatility, non-flammability, 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. Till now, many experimental data of liquid-liquid equilibrium (LLE) have been reported for the (IL + aromatic + aliphatic) systems with varying ILs [10-18], where the cations are mostly alkyl (R-) substituted imidazolium or pyridinium, while the anions are diversified including halide, PF<sub>6</sub>, BF<sub>4</sub>, dialkyl-phosphate, alkyl-sulfate, and bis{(trifluoromethyl)sulfonyl}amide etc. 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. The candidate IL for the separation of aromatic/aliphatic mixture is better composed of an aromatic cation, e.g. R-substituted imidazolium or pyridinium, and an appropriate anion that makes the ILs suitable for practical uses. 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 and low cost. Additionally the transition-metal containing ionic liquids were applied in different purpose as catalysis, reactions media, etc., but in the separation of aromatic/aliphatic mixture to date are not reported. In this regard, the feasibility of use the imidazolium or pyridinium as cations and transition-metal ions,  $[\text{FeCl}_3]$ ,  $[\text{AlCl}_3]$ , as anion, is worthy of study. The following ionic liquids 1-butyl-3-methylimidazolium tetrachloroferrate ( $[\text{Bmim}][\text{FeCl}_4]$ ), 1-butyl-3-methylimidazolium tetrachloroaluminate ( $[\text{Bmim}][\text{AlCl}_4]$ ), N-butylpyridinium tetrachloroferrate ( $[\text{BuPy}][\text{FeCl}_4]$ ), N-butylpyridinium tetrachloroaluminate ( $[\text{BuPy}][\text{AlCl}_4]$ ), were prepared and investigated in this study. Besides, the LLE data for the present ILs with aromatic (benzene) and aliphatic (cyclohexane) 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 +  $[\text{BMIM}][\text{FeCl}_4]$ }, {cyclohexane + benzene +  $[\text{Bmim}][\text{AlCl}_4]$ }, and {cyclohexane + benzene +  $([\text{BuPy}][\text{FeCl}_4])$ }, {cyclohexane + benzene +  $([\text{BuPy}][\text{AlCl}_4])$ }, and the experimental data were correlated by the non-random two-liquid (NRTL) model.

## 2. Experimental

### 2.1. Materials

The chemicals used in this study were all received from different sources, of which benzene, cyclohexane, and toluene are with a nominal minimum mass fraction of 0.995. N-methylimidazole, pyridine, 1-chlorobutane, anhydrous iron chloride, anhydrous aluminum chloride, diethyl ether, and ethanol anhydrous are of AR grade reagents and were used as received.

### 2.2. Preparation of precursor ionic liquids

$[\text{Bmim}]\text{Cl}$  was synthesized by refluxing the mixture of N-methylimidazole and chlorobutane at  $90\text{ }^\circ\text{C}$  for 12h with ca. 10% excess stoichiometric chlorobutane. The excessive reactants of the raw product was removed firstly by rotary evaporation under reduced pressure and then washed three times with equal volume of diethyl ether. The resulting white precipitate, i.e.  $[\text{BMIM}]\text{Cl}$  at room temperature, was filtrated and dried in a vacuum oven. The same procedures was used for the preparation of  $[\text{BuPy}]\text{Cl}$ .

### 2.3. Preparation of final ionic liquids

$[\text{BMIM}][\text{FeCl}_4]$  was prepared by mixing equal moles of anhydrous iron chloride and  $[\text{BMIM}]\text{Cl}$ . The mixture was left stirring overnight at room temperature, and then treated by a rotary evaporator to remove any residual volatile impurities, the other ionic liquids  $[\text{BMIM}][\text{AlCl}_4]$ ,  $[\text{BuPy}][\text{FeCl}_4]$ , and  $[\text{BuPy}][\text{AlCl}_4]$  were prepared with the same procedures. The structure of the ILs investigated was confirmed in terms of  $^1\text{H NMR}$  spectrum and no other impurities were observed. Therefore, the purity of the all ionic liquids investigated in this study was above 0.980 in mole fraction in terms of NMR and elementary analysis, and the water mass fraction was less than  $4 \times 10^{-4}$  as measured by the Karl-Fischer method (CBS-1A).

### 2.4. Apparatus and Procedures

The LLE measurement was conducted in a jacketed glass cell of about 150ml sealed by a silicon rubber cap. The equilibrium liquid temperature was maintained by circulating water coming from a super thermostat with temperature fluctuation within ( $\pm 0.1\text{ }^\circ\text{C}$ ). The relative composition of the binary mixtures, i.e. (benzene and cyclohexane), in the pretreated samples was analyzed using gas chromatography (SHIMADZU GC2010 equipped with a FID detector and FFAP capillary column,  $30\text{m} \times 0.25\text{mm.i.d} \times 5\mu\text{m}$ ; carrier gas  $\text{N}_2$ ; temperature program: ( $70$  to  $170\text{ }^\circ\text{C}$ ) at  $10\text{ }^\circ\text{C min}^{-1}$  and then maintained at  $170\text{ }^\circ\text{C}$  for 30min.

## 3. Results and Discussion

The (Liquid + liquid) equilibrium (LLE) data were measured for four ternary systems of (Cyclohexane + Benzene + Ionic Liquid) at  $T = 298.15\text{K}$  and atmospheric pressure. The resulting phase diagrams

for the four ternary systems are shown in Figures 3.1 to 3.4. As seen from Figures 3.1 to 3.4, 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. 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 3.1 to 3.4.

**Table 3.1:** LLE Data in Mole Fraction for {cyclohexane (1) + benzene (2) + [BMIM][FeCl<sub>4</sub>](3)} System at 298.15K along with the Selectivity (S) and Distribution Factor of Benzene (D).

alkane-rich phase		IL-rich phase		S	D
$x'_1$	$x'_2$	$x''_1$	$x''_2$		
0.9705	0.0295	0.1811	0.0636	11.55	2.16
0.9286	0.0714	0.1642	0.1280	10.14	1.79
0.8128	0.1872	0.1488	0.2848	8.31	1.52
0.6664	0.3336	0.1307	0.4258	6.51	1.28
0.5241	0.4759	0.1233	0.5299	4.73	1.11
0.4204	0.5796	0.1133	0.5826	3.73	1.01

**Table 3.2:** LLE Data in Mole Fraction for {cyclohexane (1) + benzene (2) + ([Bmim][AlCl<sub>4</sub>](3)} at 298.15K along with the Selectivity (S) and Distribution Factor of Benzene(D).

alkane-rich phase		IL-rich phase		S	D
$x'_1$	$x'_2$	$x''_1$	$x''_2$		
0.9725	0.0275	0.2158	0.0619	10.12	2.25
0.9466	0.0534	0.2093	0.1171	9.92	2.19
0.838	0.1620	0.1905	0.2884	7.83	1.78
0.7139	0.2861	0.1644	0.4240	6.44	1.48
0.4752	0.5248	0.1239	0.5880	4.30	1.12

**Table 3.3:** LLE Data in Mole Fraction for {cyclohexane (1) + benzene (2) + ([Bmim][AlCl<sub>4</sub>](3)} at 298.15K along with the Selectivity (S) and Distribution Factor of Benzene(D).

alkane-rich phase		IL-rich phase		S	D
$x'_1$	$x'_2$	$x''_1$	$x''_2$		
0.9659	0.0341	0.2001	0.0730	10.33	2.14
0.9380	0.0620	0.2024	0.1218	9.10	1.96
0.8188	0.1812	0.1814	0.2987	7.44	1.65
0.6948	0.3052	0.1605	0.4234	6.01	1.39
0.4422	0.5578	0.1255	0.5850	3.69	1.05

**Table 3.4:** LLE Data in Mole Fraction for System {cyclohexane (1) + benzene (2) + ([BuPy][AlCl<sub>4</sub>](3)} at 298.15K along with the Selectivity (S) and Distribution Factor of Benzene(D).

alkane-rich phase		IL-rich phase		S	D
$x'_1$	$x'_2$	$x''_1$	$x''_2$		
0.9684	0.0316	0.2422	0.0693	8.77	2.19
0.7027	0.2973	0.1476	0.4654	7.45	1.57
0.4752	0.5248	0.1239	0.5880	4.30	1.12

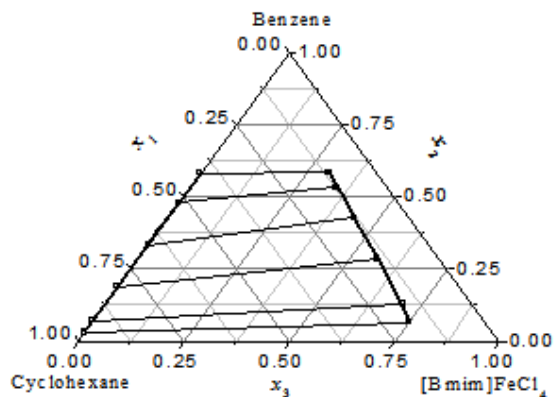
The values of S and D were calculated by virtue of the experimental LLE data using Equations 3.1 and 3.2 below.

$$S = \frac{(x''_2/x''_1)}{(x'_2/x'_1)} \quad (3.1)$$

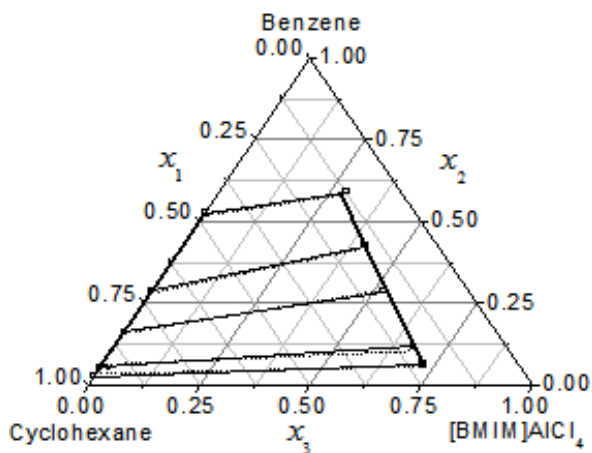
$$D = \frac{(x''_2)}{(x'_2)} \quad (3.2)$$

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.

In order to compare the selectivity of different ILs for the benzene from the cyclohexane, the selectivity for the four ternary systems studied here is presented in Figure 3.5. By analyzing this Figure, some conclusions can be drawn.

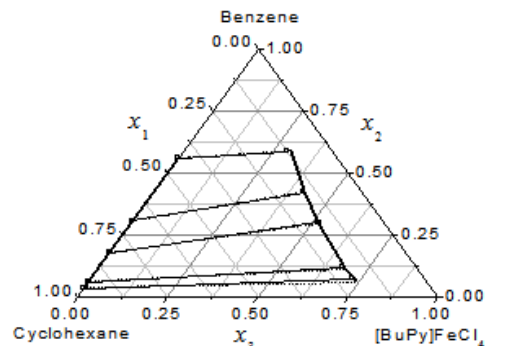


**Figure 3.1:** Binodal curves and tie-lines for the ternary mixture {cyclohexane (1) + benzene (2) + [Bmim][FeCl<sub>4</sub>] (3)} at 298.15K. —, Predicted line by the NRTL equation; experimental data.

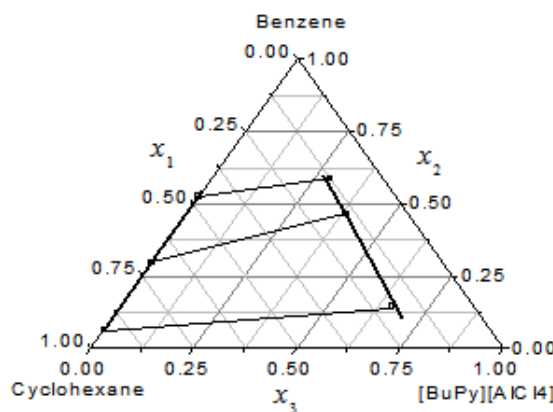


**Figure 3.2:** Binodal curves and tie-lines for the ternary mixture {cyclohexane (1) + benzene (2) + [Bmim][AlCl<sub>4</sub>] (3)} at 298.15K. Predicted line by the NRTL equation; experimental data.

First, the selectivity values for all the systems studied are higher than unity. This indicates that all ILs show a preferential extracting ability for the benzene from the cyclohexane binary mixtures, which may be ascribed to the specific  $\pi$ - $\pi$  electron interaction between benzyl ring and the aromatic imidazolium and pyridinium cations and of the anions involved in the ILs.



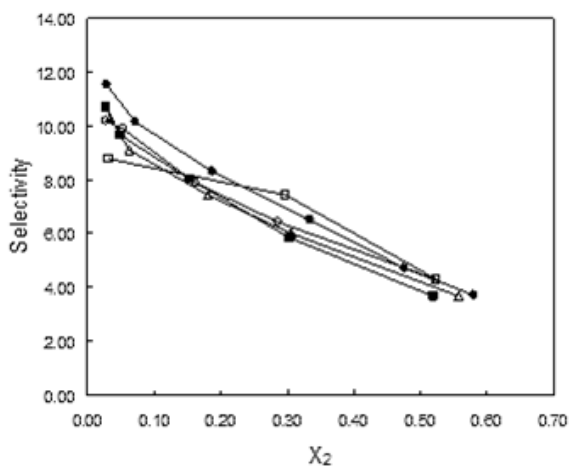
**Figure 3.3:** Binodal curves and tie-lines for the ternary mixture {cyclohexane (1) + benzene (2) + [BuPy][FeCl<sub>4</sub>] (3)} at 298.15K. Predicted line by the NRTL equation; experimental data.



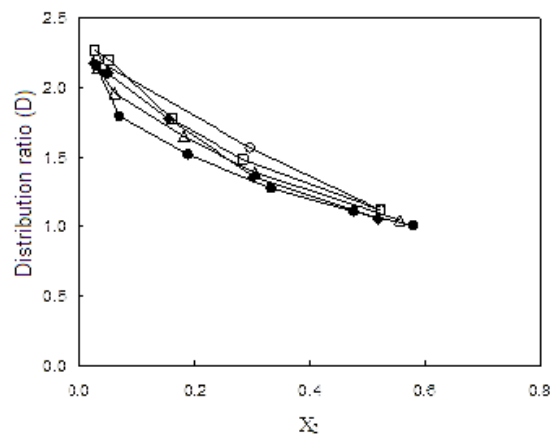
**Figure 3.4:** Binodal curves and tie-lines for the ternary mixture {cyclohexane (1) + benzene (2) + [BuPy][AlCl<sub>4</sub>] (3)} at 298.15K. Predicted line by the NRTL equation; experimental data.

Second, the LLE data measurement for the ternary systems were all conducted at 298.15K, therefore interestingly, 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. Third, the selectivity always decreases with the increase of the concentration of aromatic component in the raffinate for all 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  $\gamma_{2,aliphatic}^{\infty}/\gamma_{2,IL}^{\infty}$  as derived from Equation 3.1. Finally, the selectivity of all ILs for benzene from the binary mixture (benzene + cyclohexane) at fixed conditions follows the

order,  $[Bmim][FeCl_4] > [BuPy][FeCl_4] > [Bmim][AlCl_4] > [BuPy][AlCl_4]$ . The extraction selectivity of ILs  $[BMIM][FeCl_4]$  and  $[BuPy][FeCl_4]$  is a little higher than the other ILs 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 introduce additional electron donor-acceptor interaction between IL and the benzyl ring, leading to a higher selectivity for the aromatic components. Moreover,  $[FeCl_3]$  based-ILs investigated here are a hydrophobic IL with much lower viscosity and melting temperature in comparison with  $[Bmim][AlCl_4]$ , and thus advantageous as a promising candidates for the aromatic extraction process.



**Figure 3.5:** Selectivity of IL for benzene versus mole fraction of benzene in the raffinate phase ( $x_2$ ) for the ternary systems {cyclohexane + benzene + IL} at 298.15K, Legend: Symbols are experimental data for different ILs: (●),  $[BMIM][FeCl_4]$ ; (○),  $[BMIM][AlCl_4]$ , at 298.15K; (△),  $[BPy][FeCl_4]$ ; (□),  $[BPy][AlCl_4]$  at 325.15K.



**Figure 3.6:** Distribution factor of benzene between different extractants and the raffinate phases, as a function of the mole fraction ( $x_2$ ) for the ternary systems {cyclohexane + benzene + IL} at 298.15K Legend: Symbols are experimental data for different ILs: (●),  $[BMIM][FeCl_4]$ ; (□),  $[BMIM][AlCl_4]$ ; (△),  $[BPy][FeCl_4]$ ; (○),  $[BPy][AlCl_4]$ .

The distribution factor of benzene between ILs and the cyclohexane phase for different ternary systems is presented in Figure 3.6. By analysis Figure 3.6, it is obvious that the ILs with  $[FeCl_4]$  and  $[AlCl_4]$  anions shows a much higher extracting capacity than IL with other transition metals anion, since the distribution factor of the benzene between ILs with  $[FeCl_4]$  and  $[AlCl_4]$  anions and cyclohexane phase is about two to four times higher than that between IL with other transition metals and cyclohexane phase. The higher extraction capacity of  $[FeCl_3]$  and  $[AlCl_3]$  based-IL coincides with the larger interionic distance among large cations and anions in comparison with other transition metals based-IL, leading to a higher filling capacity for aromatic molecules. The extracting capacity of ILs for benzene-cyclohexane mixture follows the order  $[Bmim][AlCl_4] > [Bmim][FeCl_4] > [BuPy][FeCl_4] > [BuPy][AlCl_4]$  and little difference as the selectivity order, which may be closely related to the solubility of benzene and cyclohexane in the different ILs. Moreover, in comparison with  $[Bmim][AlCl_4]$ , the ionic liquids  $[BMIM][FeCl_4]$ ,  $[BuPy][FeCl_4]$ , are a hydrophobic room temperature ionic liquids with good affinity of  $FeCl_3$  to benzene, fluidity, stability, ease of preparation, and the important are insensitivity to water.

To show the excellent performance of ILs investigated for aromatic extraction, the selectivity and

**Table 3.5:** 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 <sub>6</sub> ]	Benzene/cyclohexane	295.15	0.66	3.1	(12)
[MMIM][DMP]	Benzene/cyclohexane	295.15	-	3.6	(13)
[EMIM][DEP]	Benzene/cyclohexane	295.15	-	3.7	(13)
[BMIM][FeCl <sub>4</sub> ]	Benzene/cyclohexane	295.15	2.16	11.55	(this work)
[BMIM][AlCl <sub>4</sub> ]	Benzene/cyclohexane	295.15	2.25	10.12	(this work)
[BPy][FeCl <sub>4</sub> ]	Benzene/cyclohexane	295.15	2.16	11.55	(this work)
[BPy][AlCl <sub>4</sub> ]	Benzene/cyclohexane	295.15	2.27	13.26	(this work)
[OMIM]Cl	Benzene/cyclohexane	295.15	0.69	5.7	(10)
[OMIM]Cl	Toluene/heptane	313.15	0.43	7.7	(17)
[BMIM][BF <sub>4</sub> ]	Benzene/cyclohexane	323.15	0.56	15.9	(11)
[BMIM][BF <sub>4</sub> ]	Toluene/heptane	323.15	0.42	29.5	(18)

**Table 3.6:** NRTL Binary Parameters Regressed from LLE Data and the Fitting Deviation in ARD for the ternary Mixtures {aliphatic (1) + aromatic (2) + ILs (3)}.

component	NRTL parameters		ARD	
(i) + (j)	$a_{ij}$	$\frac{(g_{ij} - g_{ji})}{(J \text{ mol}^{-1})}$	$\frac{(g_{ji} - g_{ii})}{(J \text{ mol}^{-1})}$	
cyclohexane (1)+benzene (2)	0.45	5877.7	178.05	
		[BMIM][FeCl <sub>4</sub> ]		
cyclohexane (1) + ILs (3)	0.168	7906.897	837.375	
benzene (2) + ILs (3)	0.6047	18903.19	4968.146	0.00014
cyclohexane (1)+benzene( 2)	0.11	-5756	9932	
		[BMIM][AlCl <sub>4</sub> ]		
cyclohexane (1) + ILs (3)	0.2955	2726.535	5388.016	
benzene (2) + ILs (3)	0.3498	20884.49	-2861.71	0.000085
cyclohexane (1)+benzene (2)	0.11	-5756	9932	
		[BuPy][FeCl <sub>4</sub> ]		
cyclohexane (1) + ILs (3)	0.3189	2337.116	6684.420	
benzene (2) + ILs (3)	0.2247	37968.988	-3012.827	0.000058
cyclohexane (1)+benzene (2)	0.45	5877.7	178.05	
		[BuPy][AlCl <sub>4</sub> ]		
cyclohexane (1) + ILs (3)	0.2994	11785.92	3001.321	
benzene (2) + ILs (3)	0.4292	90749976	11071.64	0.000146
Overall ARD = 0.0001				

distribution factor values for several ILs reported till now was collected and compared in Table 3.5. It is shown that the imidazolium and pyridinium based ILs with  $[\text{FeCl}_4]$  and  $[\text{AlCl}_4]$  anions show an excellent combination of both selectivity and distribution factor in comparison with other ILs [10-13,17,18], for example,  $[\text{BMIM}][\text{BF}_4]$  has a little higher selectivity for aromatic component but its extraction capacity is much lower than the  $[\text{FeCl}_3]$  and  $[\text{AlCl}_3]$  based-ILs investigated. Further, the higher aromatic selectivity is only found for the ILs with  $[\text{BF}_4]$ ,  $[\text{FeCl}_4]$ , and  $[\text{AlCl}_4]$  anions, which may be associated with their stronger Lewis acidity than the corresponding halide anions, i.e. F and Cl, and other anions like  $[\text{PF}_6]$  and dialkylphosphates, e.g.  $[\text{DMP}]$  and  $[\text{DEP}]$ .

### 3.1. Tie-line correlation

For correlating the experimental LLE data of the ternary systems, the NRTL model of non-electrolyte solutions developed by Renon and Prausnitz [19] 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 Levenberg–Marquardt (LM) algorithm via minimization of the following objective function (OF):

$$OF = \sum_i^{NP} \left[ \left( x'_{1i} \gamma'_{1i} - x''_{1i} \gamma''_{1i} \right)^2 \right] \quad (3.3)$$

$$\left( x'_{2i} \gamma'_{2i} - x''_{2i} \gamma''_{2i} \right)^2$$

where NP is the number of data points, '1' and '2' are component 1 and 2 for a ternary system, respectively; the superscripts ' ' and ' ' refer to top and bottom phase in equilibrium respectively, and 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 (ARD), given by Equation 3.4.

$$ARD = \frac{1}{6NP} \sum_i^m \sum_j^{n-1} \left( x'_{ij} \gamma'_{ij} - x''_{ij} \gamma''_{ij} \right)^2 \quad (3.4)$$

Here, "m" and "n" are the number of tie line and component for ternary system, and NP is the number of data points. 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) was set at a value of  $\alpha_{ij} = 0.11, 0.4$  or  $0.45$ . Figures 3.1 to 3.4 showed the experimental LLE data for studied ternary systems {benzene (1) + cyclohexane (2)+ ILs (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 overall ARD justified the applicability of the NRTL model for the representation of the LLE data for the IL-containing ternary systems studied here.

## 4. Conclusion

The performances of ILs prepared from  $[\text{BMIM}]\text{Cl}$ , and  $[\text{BuPy}]\text{Cl}$  salts and the Lewis acidic anions,  $\text{FeCl}_3$  or  $\text{AlCl}_3$ , with the ratios ( $\text{FeCl}_3/[\text{BMIM}]\text{Cl} = 1$ ), ( $\text{AlCl}_3/[\text{BMIM}]\text{Cl} = 1$ ), and ( $\text{FeCl}_3/[\text{BuPy}]\text{Cl} = 1$ ), ( $\text{AlCl}_3/[\text{BuPy}]\text{Cl} = 1$ ), were tested for the separation of benzene from benzene/cyclohexane mixture. However, the extraction ability of these ILs were significantly lower than that of the corresponding  $\text{FeCl}_3$ -based IL. The reason for the higher extraction ability of  $\text{FeCl}_3$ -based ILs is likely that the fluidity and affinity of  $\text{FeCl}_3$  to benzene. Moreover a promising ionic liquid  $\text{FeCl}_3$ -based ILs is found for the extractive separation of benzene-cyclohexane mixture for its both higher selectivity and capacity for the benzene component studied, along with its favorable attributes, e.g. ease of preparation and cheapness, good fluidity and stability. The extractive selectivity of the ILs for all the studied systems shows the order of  $[\text{Bmim}][\text{FeCl}_4] > [\text{BuPy}][\text{FeCl}_4] > [\text{Bmim}][\text{AlCl}_4] > [\text{BuPy}][\text{AlCl}_4]$ , being consistent with other ILs reported with the same cation but different anions. The higher extraction selectivity of  $[\text{FeCl}_3]$ -based ILs 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 overall ARD deviation being about 0.0001.

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