Liquid Extraction of Benzene from Its Mixtures Using 1-Ethyl-3-methylimidazolium Ethylsulfate as a Solvent

Emilio J. González,[†] Noelia Calvar,*[,‡] Begoña González,[†] and Ángeles Domínguez[†]

Departamento de Ingeniería Química de la Universidad de Vigo, 36310 Vigo, Spain, and Laboratory of Separation and Reaction Engineering, Departamento de Engenharia Quimica, Facultade de Engenharia, Universidade de Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

In this work, the separation of benzene from cycloalkanes (cyclohexane, methylcyclohexane, and cyclooctane) was investigated by liquid extraction using the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate, [EMim][ESO_4]. The liquid−liquid equilibrium (LLE) data were measured for the ternary systems formed by cycloalkane, benzene, and [EMim][ESO_4] at 298.15 K and atmospheric pressure. The cloud point method was used to determine the solubility curve data, and the tie-line compositions were obtained by density measurements. The selectivity, the percent removal of aromatic, and the solute distribution ratio were calculated from the experimental LLE data. Selectivity and solute distribution ratio values were compared to those previously reported with other ionic liquids and sulfolane. Moreover, the influence of the size of the cycloalkane on the aromatic extraction was analyzed. The reliability of the experimental LLE data was tested using the Othmer−Tobias equation, and the NRTL and UNIQUAC models were used to correlate the experimental LLE data.

Introduction

Nowadays, aromatics are obtained almost exclusively from naphtha, which are combined with other nonaromatic hydrocarbons, mainly aliphatic and naphthenic compounds. The separation of aromatic hydrocarbons from aliphatic and naphthenic compounds is complicated because these compounds have very close boiling points, and several combinations form azeotropes.[1] Since conventional distillation is not suitable, the recommended process for these separations is liquid extraction using organic compounds as solvent. Industrially, the most used solvents are sulfolane (Shell Process), polyethylene glycols (UDEX Process), tetraethylene glycol (Union Carbide Process), dimethylsulfoxide (DMSO Process), *N*-methylpyrrolidone (Arosolvan Process), *N*-formylmorpholidone (Formex Process), etc.[2] Although these processes are highly optimized and offer high yields, they have a disadvantage because they are toxic and harmful to the environment. For this reason, and according with the principles of Green Chemistry,[3] it is necessary to develop new solvents that allow an effective separation and cause less damage to the environment.

Over the last 10 years, ionic liquids (ILs) have received great attention as green solvents, and they were suggested as an alternative to traditional organic solvents for liquid extraction. The ILs are organic salts with high thermal stability and a wide temperature range for the liquid phase. Moreover, since ILs have negligible vapor pressure at moderate temperature and pressure, their recovery is easier.

To understand the role of ILs in separation processes, liquid−liquid equilibrium (LLE) data are necessary. In the last years, several groups have published LLE data for the ternary systems aliphatic compound + aromatic compound + ionic liquid.[4−14] Nevertheless, only a few publications report LLE data for systems containing cycloalkanes.[11−14]

This work is a continuation of our research on the extraction of aromatic compounds from aliphatic/aromatic mixtures using ILs as a solvent. In previous papers,[15−17] the extraction of aromatic hydrocarbons from cycloakanes using a pyridinium-based ionic liquid as solvent was tested. As the results were good, the research was expanded to the separation of these compounds using an imidazolium-based ionic liquid.

In this work, the solubility curves and tie-line data for the ternary systems (cycloalkane (1) + benzene (2) + 1-ethyl-3-methylimidazolium ethylsulfate (3)) were determined at 298.15 K and atmospheric pressure. The cycloalkanes used in this work are cyclohexane, methylcyclohexane, and cyclooctane. From the experimental data, the selectivity (S), the percent removal of aromatic, and the solute distribution ratio (β) were calculated. The values of selectivity and solute distribution ratio for the system containing cyclohexane were compared with literature data for other ILs and sulfolane. Moreover, comparing the three studied systems, the influence of the size of the cycloalkane on the aromatic separation was analyzed.

The reliability of the experimentally measured LLE data was tested by the Othmer−Tobias[18] equation. Finally, the LLE data were correlated by NRTL[19] and UNIQUAC[20] models.

Experimental Section

Chemicals. Benzene, cyclohexane, methylcyclohexane, and cyclooctane were supplied by Sigma-Aldrich with purity higher than 99.9 %, 99.9 %, 99.9 %, and 99.0 % by mass, respectively. Cycloalkanes were degassed ultrasonically and dried over molecular sieves type 4 Å, supplied by Aldrich, and kept in an inert argon atmosphere to avoid moisture.

The ionic liquid used in this work was synthesized in our laboratory following the procedure previously detailed.[21] To ensure its purity, an ^{1}H NMR was made. The purity of 1-ethyl-

---

* To whom correspondence should be addressed. E-mail: noecs@uvigo.es. Tel.: +34 986 812 422. Fax: +34 986 812 382.

[†] Universidad de Vigo.

[‡] Universidade de Porto.

10.1021/je100508y

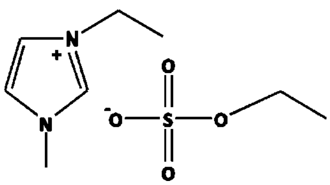

Figure 1. Structure of the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate, [EMim][ESO$_4$].

Table 1. Density (ρ) and Refractive Index (n_D) of Pure Components at T = 298.15 K

	ρ/(g·cm^{-3})		n_D	
component	exp.	lit.	exp.	lit.
[EMim][ESO$_4$]	1.23723	1.23817[a] 1.23693[b]	1.47910	1.47903[a]
benzene	0.87357	0.87360[c]	1.49774	1.49792[c]
cyclohexane	0.77380	0.77389[c]	1.42360	1.42354[c]
methylcyclohexane	0.76502	0.76506[c]	1.42062	1.42058[c]
cyclooctane	0.83147	0.83151[d]	1.45598	1.4560[e]

[a] From ref 22. [b] From ref 23. [c] From ref 24. [d] From ref 25. [e] From ref 26.

3-methylimidazolium ethylsulfate, [EMim][ESO$_4$], was found to be higher than 99 % by mass. The structure of this ionic liquid is presented in Figure 1.

The ionic liquid was kept in bottles with inert gas. Before use, the ionic liquid was treated by vacuum evaporation (p/Pa = 0.2) and moderate temperature (T/K = 323.15) for several days to remove possible residual volatile impurities and moisture. The water content was determined using a 787 Karl Fischer Titrino, and ionic liquid showed a mass fraction of water less than $6 \cdot 10^{-4}$.

The physical properties (density and refractive index) of the pure components and literature data[22−26] at 298.15 K are listed in Table 1. The small differences between experimental and literature data may be due to the presence of water or nonvolatile impurities in our samples or their samples.

Apparatus and Procedure. In the current work, several apparatuses have been used for the preparation of samples and the determination of properties. For the preparation of samples, a Mettler AX-205 Delta Range balance with an uncertainty of $\pm 3 \cdot 10^{-4}$ g was used, and an Anton Paar DSA-5000 digital vibrating tube densimeter with an uncertainty of $\pm 3 \cdot 10^{-5}$ g·cm^{-3} and an automatic refractometer (Abbemat-HP, Dr. Kernchen) with an uncertainty in the experimental measurements of $\pm 4 \cdot 10^{-5}$ were used for the measurement of densities and refractive indices, respectively.

For the study of the liquid−liquid equilibria of the ternary systems, the solubility curves and the tie-line compositions were determined at 298.15 K. The temperature was maintained constant in a thermostatic bath (PoliScience Digital Temperature Controller) with a precision of ± 0.01 K and controlled with a digital thermometer ASL model F200 with an uncertainty of ± 0.01 K. The detailed procedure has been explained in a previous work.[15] Briefly, the solubility curves were performed by the cloud point method, and a polynomial expression was obtained by measuring the density of each solubility point of known composition.

To estimate the error of the technique used for the determination of solubility curves, three validation points were evaluated. To perform the validation points, three samples were prepared by weighing (following the same procedure as that for the preparation of the solubility points), and the densities were measured. By means of the above-mentioned polynomial expression, and using the experimental density values, calculated compositions were obtained. Comparing the experimental and calculated compositions, the maximum error was estimated to be ± 0.006 in mole fraction.

Table 2. Experimental Liquid−Liquid Equilibrium Data in Mole Fraction for Ternary Systems Cycloalkane (1) + Benzene (2) + [EMim][ESO$_4$] (3) at T = 298.15 K, % Removal of Aromatic (Mass Basis), Solute Distribution Ratio, β, and Selectivity, S, Values

cycloalkane-rich phase		ionic liquid-rich phase				
x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}	% removal of aromatic	β	S
Cyclohexane (1) + Benzene (2) + [EMim][ESO$_4$] (3)						
0.946	0.054	0.030	0.034	13.6	0.63	19.85
0.890	0.110	0.031	0.061	13.5	0.55	15.92
0.834	0.166	0.031	0.084	12.5	0.51	13.61
0.777	0.223	0.030	0.112	13.4	0.50	13.01
0.651	0.349	0.026	0.171	14.5	0.49	12.27
0.530	0.470	0.021	0.222	15.2	0.47	11.92
0.409	0.591	0.017	0.273	15.5	0.46	11.11
0.274	0.726	0.011	0.330	16.1	0.45	11.32
0.138	0.862	0.006	0.389	17.7	0.45	10.38
Methylcyclohexane (1) + Benzene (2) + [EMim][ESO$_4$] (3)						
0.943	0.057	0.015	0.036	17.2	0.63	39.71
0.886	0.114	0.014	0.067	16.5	0.59	37.19
0.834	0.166	0.013	0.095	15.5	0.57	36.71
0.775	0.225	0.013	0.122	15.5	0.54	32.32
0.774	0.226	0.012	0.122	15.5	0.54	34.82
0.656	0.344	0.011	0.175	15.4	0.51	30.34
0.530	0.470	0.010	0.224	15.6	0.48	25.26
0.410	0.590	0.008	0.271	15.5	0.46	23.54
0.273	0.727	0.007	0.323	16.2	0.44	17.33
0.147	0.853	0.005	0.374	16.8	0.44	12.89
Cyclooctane (1) + Benzene (2) + [EMim][ESO$_4$] (3)						
0.899	0.101	0.011	0.055	9.6	0.54	44.50
0.842	0.158	0.012	0.085	11.1	0.54	37.75
0.840	0.160	0.011	0.086	12.0	0.54	41.05
0.786	0.214	0.011	0.112	12.1	0.52	37.40
0.663	0.337	0.011	0.174	15.2	0.52	31.12
0.535	0.465	0.010	0.219	15.2	0.47	25.20
0.412	0.588	0.010	0.270	15.3	0.46	18.92
0.284	0.716	0.009	0.321	16.1	0.45	14.15
0.154	0.846	0.006	0.378	17.0	0.45	11.47

For the tie-line determination, mixtures of known compositions inside the immiscible region were introduced into glass cells and closed with silicon covers. Mixtures were agitated using a magnetic stirrer for 6 h to allow an intimate contact between phases, and then the equilibrium phases were left overnight to settle down. A sample from each phase was withdrawn using a syringe, and their densities were measured. By means of the polynomial expressions previously determined, compositions of the tie-line ends were calculated. It is important to mention that, since it was found that the IL is immiscible in the pure studied components (cycloalkanes and benzene) and in the binary mixtures cycloalkane + benzene, the presence of ionic liquid in the cycloalkane-rich phase was assumed zero, and the composition of this phase was determined using the values of density versus molar fraction for the binary systems cycloalkane (1) + benzene (2).

Results and Discussion

The compositions of the determined solubility curves for the ternary systems cycloalkane (1) + benzene (2) + [EMim][ESO$_4$] (3) at 298.15 K are given in Table S1, available in the Supporting Information. The values of the density versus mole fraction for the binary systems cycloalkane (1) + benzene (2) at 298.15 K were taken from a previous work.[27]

The experimental compositions of the tie-line ends, obtained at 298.15 K and atmospheric pressure, are presented in Table 2 for the three ternary systems. As mentioned above, the cycloalkane-rich phases were assumed to be totally free of IL, and it was confirmed after ^{1}H NMR analysis of some hydrocarbon-rich phases. This assumption is also concluded by other authors studying LLE of systems with different ionic liquids.[9,28,29] The immiscibility of IL in cycloalkane + benzene mixtures has the advantage that the recovery of IL is easier. Figure 2 shows the ternary diagrams of the experimental tie-lines of the studied ternary systems. Note that two tie-lines with similar initial compositions were carried out for the LLE of each of the ternary systems methylcyclohexane (1) or cyclooctane (1) + benzene (2) + [EMim][ESO$_4$] (3), showing the repeatability of the experiments. Inspection of Figure 2 and Table 2 indicates that the immiscible region increases as the number of carbon atoms in the cycloalkane increases, in the order cyclooctane > methylcyclohexane > cyclohexane. It can also be observed that the tie-lines for all the studied systems present a negative slope, and this slope is more negative as the composition in benzene increases.

Table 2 also includes the corresponding values for the percent removal of aromatic expressed as 100·(amount of benzene extracted in the IL-rich phase divided by the total amount of benzene extracted in the two phases), the solute distribution ratio, β, and the selectivity, S, defined below

$$\beta = \frac{x_2^{\mathrm{II}}}{x_2^{\mathrm{I}}} \tag{1}$$

$$S = \frac{x_2^{\mathrm{II}} x_1^{\mathrm{I}}}{x_2^{\mathrm{I}} x_1^{\mathrm{II}}} \tag{2}$$

where x_1^{I} and x_2^{I} are the mole fractions of cycloalkane and benzene, respectively, in the upper phase (cycloalkane-rich phase), and x_1^{II} and x_2^{II} are the mole fractions of cycloalkane and benzene, respectively, in the lower phase (IL-rich phase).

As seen in Table 2, the experimental selectivity and solute distribution ratio values decrease as the composition of the benzene in the raffinate phase increases. The selectivity values of the systems containing cyclooctane and methylcyclohexane are higher than those obtained for the system with cyclohexane, while the values of the solute distribution ratio and percent removal of aromatic are almost similar for the three systems. It can be inferred from the selectivity values that the size of the hydrocarbon has an influence on the selectivity: the larger the cycloalkane, the higher the selectivity (cyclooctane > cyclohexane), and similar results are achieved for the systems containing cyclooctane (a high cycloalkane) and methylcyclohexane (a cycloalkane with a side chain). This behavior is also

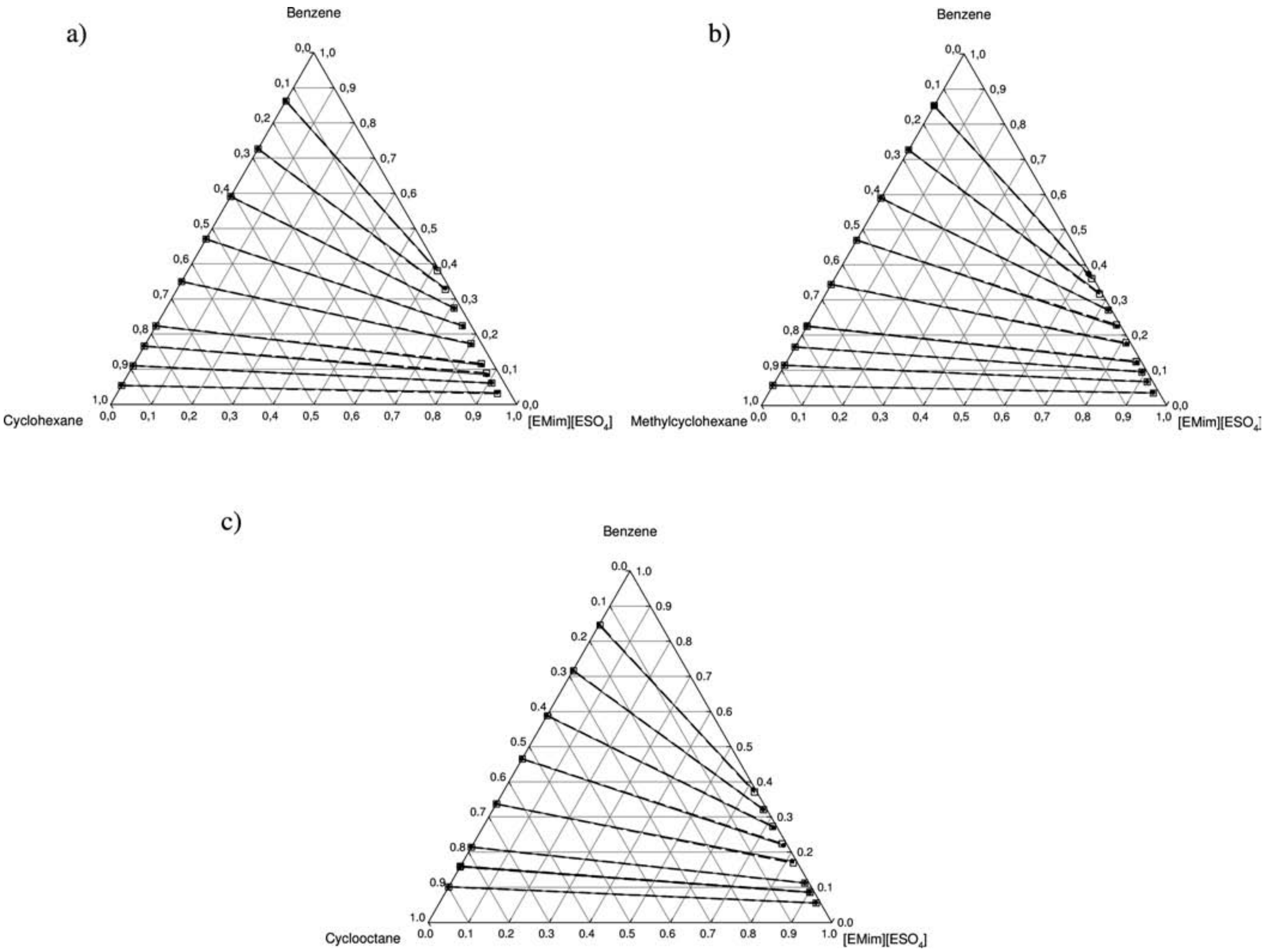

Figure 2. LLE of the ternary systems (a) cyclohexane (1) + benzene (2) + [EMim][ESO$_4$] (3); (b) methylcyclohexane (1) + benzene (2) + [EMim][ESO$_4$] (3); and (c) cyclooctane + benzene (2) + [EMim][ESO$_4$] (3) at T = 298.15 K. Solid lines and full points indicate experimental tie-lines, and dashed lines and empty squares indicate calculated data from the NRTL model.

present when the systems contain lineal alkanes instead of cycloalkanes.[30]

All values of the selectivity for the studied systems are higher than unity, which confirms that the aromatic extraction is possible with [EMim][ESO$_4$]. Nevertheless, considering the type of ternary diagrams and that a small variation in the compositions has great effect on selectivity, this parameter should be interpreted as a range. The obtained β values are always less than 1, and therefore a high amount of ionic liquid would be necessary for the extraction, although the easiness of the recovery of the IL must be considered.

The variations of S and β with the composition of benzene in the raffinate phase for the ternary system cyclohexane (1) + benzene (2) + [EMim][ESO$_4$] (3) obtained in this work, together with literature data for other ILs and sulfolane,[12−14,17,31] are presented in Figure 3. The values of S and β achieved with the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMim][PF$_6$]) are the highest, but since they only represent low compositions of benzene in the raffinate phase, the comparison is difficult. The ionic liquids with the ethylsulfate anion, 1-ethyl-3-methylpyridinium ethylsulfate ([EMpy][ESO$_4$]) and 1-ethyl-3-methylimidazolium ethylsulfate ([EMim][ESO$_4$]), give the highest selectivities. The solute distribution ratio for all the presented solvents is between 0 and 1, except for [BMim][PF$_6$] at low compositions of benzene in the raffinate, with β values higher than 2. In general, the selectivity values decrease with the increase in composition of benzene in the raffinate phase, while the composition of benzene showed very little influence on the solute distribution ratio values.

The reliability of the experimental tie-line compositions was ascertained by applying the equation provided by Othmer−Tobias[18]

$$\ln\left(\frac{1 - w_1^{\mathrm{I}}}{w_1^{\mathrm{I}}}\right) = a + b\ln\left(\frac{1 - w_3^{\mathrm{II}}}{w_3^{\mathrm{II}}}\right) \tag{3}$$

where w_1^{I} is the mass fraction of cycloalkane in the cycloalkane-rich phase; w_3^{II} is the mass fraction of the ionic liquid in the ionic liquid-rich phase; and a and b are adjustable parameters. The linearity of this fitting indicates the degree of consistency of the experimental data. The parameters obtained from the Othmer−Tobias equation are presented in Table S2, available in the Supporting Information, together with the correlation factor, R^2, and the standard error of estimate, $S_{y/x}$, for all the studied ternary systems at 298.15 K.

Thermodynamic Correlation

The nonrandom two liquid (NRTL)[19] and universal quasi-chemical (UNIQUAC)[20] models were used to correlate the LLE experimental data.

In the correlation using the NRTL model, although α_{ij} can be an adjustable parameter, in this case it was considered fixed. For each system, several values for α_{ij} were tested for each system (from $\alpha_{ij} = 0$ to 0.5), and the best results were achieved for the values presented in Table 3. The objective function used minimizes the differences between the experimental and calculated mole fraction of the components in both phases. It is important to mention that only one of the repeated tie-lines from each system containing methylcyclohexane or cyclooctane was included in the correlation. The NRTL binary interaction parameters of the ternary systems correlated are listed in Table 3, as well as the standard deviations, σ.

The required van der Waals parameters, r_i and q_i, for the UNIQUAC model were taken from the literature,[22,32,33] and they are presented in Table 4. The UNIQUAC binary interaction parameters and the standard deviations are summarized in Table 5.

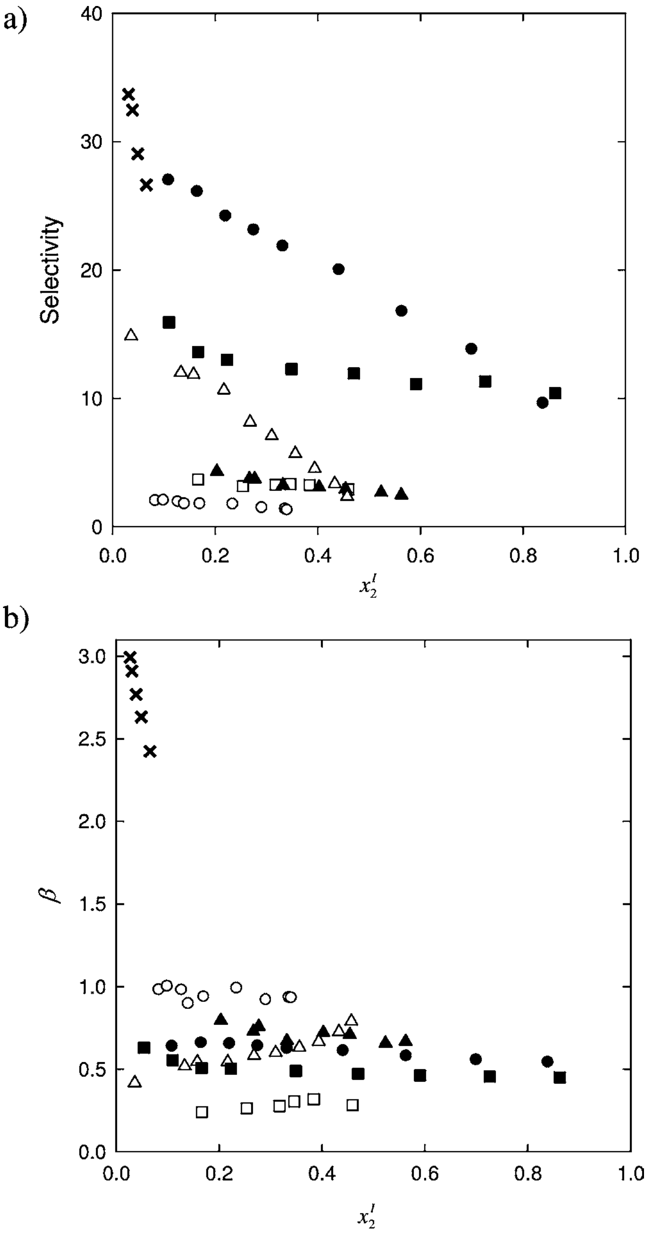

Figure 3. (a) Selectivity and (b) solute distribution ratio, for the ternary systems cyclohexane (1) + benzene (2) + solvent (3), at T = 298.15 K, as a function of the mole fraction of benzene in the cyclohexane-rich phase. Solvents: ●, [EMpy][ESO$_4$] (from ref 17); □, [MMim][DMP] (from ref 12); ▲,[EMim][DEP](from ref 12); ○, [Mim][DBP] (from ref 13); Δ, sulfolane (from ref 31); ×, [BMim][PF$_6$] (from ref 14); ■, [EMim][ESO$_4$] (this work).

The standard deviations were calculated as follows

$$\sigma = \sqrt{\frac{\sum_{i=1}^{k}\sum_{j=1}^{N}(x_{ij}^{\mathrm{exp}} - x_{ij}^{\mathrm{calc}})^2}{6k}} \tag{4}$$

where k is the number of experimental tie-lines; N is the number of components; and x_{ij} is the molar fraction.

Both models are capable of correlating the experimental LLE data, as can be inferred from Tables 3 and 5. Figure 2 shows

Table 3. NRTL Binary Interaction Parameters and Standard Deviations for LLE Data of Ternary Systems at T = 298.15 K

$i-j$	Δg_{ij} ($\text{kJ}\cdot\text{mol}^{-1}$)	Δg_{ji} ($\text{kJ}\cdot\text{mol}^{-1}$)	α_{ij}	σ
Cyclohexane (1) + Benzene (2) + [EMim][ESO$_4$] (3)				
1−2	−3.171	2.657	0.10	0.002
1−3	1166.5	9.351		
2−3	26.047	−8.530		
Methylcyclohexane (1) + Benzene (2) + [EMim][ESO$_4$] (3)				
1−2	−4.184	7.039	0.10	0.003
1−3	62.621	5.843		
2−3	17.727	−6.443		
Cyclooctane (1) + Benzene (2) + [EMim][ESO$_4$] (3)				
1−2	−2.468	4.279	0.20	0.002
1−3	16.942	7.299		
2−3	14.937	−2.454		

Table 4. Structural Parameters for the UNIQUAC Equation

component	r_i	q_i
benzene[a]	3.188	2.400
cyclohexane[a]	4.046	3.240
methylcyclohexane[a]	4.720	3.776
cyclooctane[a]	5.395	4.320
[EMim][ESO$_4$][b,c]	7.94	7.21

[a] From ref 22. [b] From ref 32. [c] From ref 33.

Table 5. Values of the UNIQUAC Binary Interaction Parameters and Standard Deviations for LLE Data of the Ternary Systems at T = 298.15 K

$i-j$	Δu_{ij} ($\text{kJ}\cdot\text{mol}^{-1}$)	Δu_{ji} ($\text{kJ}\cdot\text{mol}^{-1}$)	σ
Cyclohexane (1) + Benzene (2) + [EMim][ESO$_4$] (3)			
1−2	−0.398	0.586	0.006
1−3	8.159	0.280	
2−3	16.163	−1.624	
Methylcyclohexane (1) + Benzene (2) + [EMim][ESO$_4$] (3)			
1−2	−0.340	1.046	0.004
1−3	678.00	0.269	
2−3	6.583	−1.241	
Cyclooctane (1) + Benzene (2) + [EMim][ESO$_4$] (3)			
1−2	1.049	−0.468	0.002
1−3	1.826	1.279	
2−3	2.437	−0.438	

the experimental LLE data plotted together with those obtained from the NRTL correlation model, where the goodness of the NRTL correlation model can be visually confirmed.

Conclusions

In this work, liquid−liquid equilibria for the ternary systems cyclohexane (1) + benzene (2) + [EMim][ESO$_4$] (3), methylcyclohexane (1) + benzene (2) + [EMim][ESO$_4$] (3), and cyclooctane (1) + benzene (2) + [EMim][ESO$_4$] (3) were determined at T = 298.15 K and atmospheric pressure. Selectivity, percent removal of aromatic, and solute distribution ratio were calculated from experimental data. The miscible region of the studied ternary systems decreases in the order cyclohexane > methylcyclohexane > cyclooctane. The selectivity values of the systems containing cyclooctane and methylcyclohexane are higher than those obtained for the system with cyclohexane, and the values of the solute distribution ratio and percent removal of aromatic are almost similar for the three systems.

The values of the selectivity for the studied systems are higher than unity, which confirms that the aromatic extraction for these systems is possible with [EMim][ESO$_4$]. The obtained β values are low, which implies that a high amount of the ionic liquid would be necessary for the extraction.

The use of the Othmer−Tobias equation ascertained the reliability of the experimental data, obtaining good results, and NRTL and UNIQUAC models were satisfactorily applied to correlate the liquid−liquid equilibrium data.

Supporting Information Available:

Solubility curves and Othmer−Tobias parameters, at 298.15 K, for the ternary systems. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Meindersma, G. W.; Podt, A.; Haan, A. B. Ternary liquid-liquid equilibria for mixtures of an aromatic + an aliphatic hydrocarbon + 4-methyl-N-butylpyridinium tetrafluoroborate. *J. Chem. Eng. Data* **2006**, *51*, 1814–1819.

(2) Rydberg, J.; Cox, M.; Musikas, C.; Choppin, G. R. *Solvent Extraction Principles and Practice, Revised and Expanded*; Dekker: New York, 2004.

(3) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: New York, 1998.

(4) Letcher, T. M.; Reddy, P. Ternary (liquid + liquid) equilibria for mixtures of 1-hexyl-3-methylimidazolium (tetrafluoroborate or hexafluoroborate) + benzene + an alkane at T = 298.2 K andp = 0.1 MPa. *J. Chem. Thermodyn.* **2005**, *37*, 415–421.

(5) Domanska, U.; Pobudkowska, A.; Zolek-Tryznowska, Z. Effect of an ionic liquid (IL) cation on the ternary system (IL + *p*-Xylene + Hexane) at T = 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 2345–2349.

(6) Maduro, R. M.; Aznar, M. Liquid-liquid equilibrium of ternary systems 1-butyl-3-methylimidazolium hexafluorophosphate + aromatic + aliphatic. *Fluid Phase Equilib.* **2008**, *265*, 129–138.

(7) Arce, A.; Earle, M. J.; Rodríguez, H.; Seddon, K. R.; Soto, A. 1-ethyl-3- methylimidazolium bis{(trifluoromethyl)sulfonyl}amide as solvent for the separation of aromatic and aliphatic hydrocarbons by liquid extraction-extension to C$_7$- and C$_8$- fractions. *Green Chem.* **2008**, *10*, 1294–1300.

(8) Pereiro, A. B.; Rodríguez, A. Application of the ionic liquid Ammoeng 102 for the aromatic/aliphatic hydrocarbon separation. *J. Chem. Thermodyn.* **2009**, *41*, 951–956.

(9) García, J.; Fernández, A.; Torrecilla, J. S.; Olier, M.; Rodríguez, F. Liquid-liquid equilibria for {hexane + benzene + 1-ethyl-3-methylimidazolium ethylsulfate} at (298.2, 313.2 and 328.2) K. *Fluid Phase Equilib.* **2009**, *282*, 117–120.

(10) Hansmeier, A. R.; Jongmans, M.; Meindersma, G. W.; de Haan, A. B. LLE data for the ionic liquid 3-methyl-N-butyl pyridinium dicyanamide with several aromatic and aliphatic compounds. *J. Chem. Thermodyn.* **2010**, *42*, 484–490.

(11) Abu-Eishah, S. I.; Dowaidar, A. M. Liquid-Liquid Equilibrium of ternary systems of cyclohexane + (benzene, + toluene, + ethylbenzene, or +o-xylene) + 4-methyl-N-butyl pyridinium tetrafluoroborate ionic liquid at 303.15 K. *J. Chem. Eng. Data* **2008**, *53*, 1708–1712.

(12) Wang, R.; Wang, J.; Meng, H.; Li, C.; Wang, Z. Liquid-liquid equilibria for benzene + cyclohexane + 1-methyl-3-methylimidazolium dimethylphosphate or + 1-ethyl-3-methylimidazolium diethylphosphate. *J. Chem. Eng. Data* **2008**, *53*, 1159–1162.

(13) Wang, R.; Li, C.; Meng, H.; Wang, J.; Wang, Z. Ternary liquid-liquid equilibria measurement for benzene + cyclohexane + *N*-methylimidazole, or *N*-ethylimidazole, or *N*-methylimidazolium dibutylphosphate at 298.2 K and atmospheric pressure. *J. Chem. Eng. Data* **2008**, *53*, 2170–2174.

(14) Lu, Y.; Yang, X.; Luo, G. Liquid-liquid equilibria for benzene + cyclohexane + 1-butyl-3-methylimidazolium hexafluorophosphate. *J. Chem. Eng. Data* **2010**, *55*, 510–512.

(15) González, E. J.; Calvar, N.; González, B.; Domínguez, A. Measurement and correlation of liquid-liquid equilibria for ternary systems {cyclooctane + aromatic hydrocarbon + 1-ethyl-3-methylpyridinium ethylsulfate} at T= 298.15 K and atmospheric pressure. *Fluid Phase Equilib.* **2010**, *291*, 59–65.

(16) González, E. J.; Calvar, N.; Canosa, J.; Domínguez, A. Effect of the chain lengh on aromatic ring in the separation of aromatic compounds from methylcyclohexane using [EMpy][ESO$_4$] ionic liquid. *J. Chem. Eng. Data* **2010**, DOI: 10.1021/je900807v.

(17) González, E. J.; Domínguez, I.; González, B.; Canosa, J. Liquid-liquid equilibria for ternary systems of {cyclohexane + aromatic compounds + 1-ethyl-3-methylpyridinium ethylsulfate}. *Fluid Phase Equilib.* **2010**, DOI: 10.1016/j.fluid.2010.05.009.

(18) Othmer, D. F.; Tobias, P. E. Tie line correlation. *Ind. Eng. Chem.* **1942**, *34*, 693–696.

(19) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamics excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.

(20) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116–128.

(21) Holbrey, J. D.; Reichert, W. M.; Swatloski, R. P.; Broker, G. A.; Pitner, W. R.; Seddon, K. R.; Rogers, R. D. Efficient, halide free synthesis of new, low cost ionic liquids: 1,3-dialkylimidazolium salts containing methyl- and ethyl- sulfate anions. *Green Chem.* **2002**, *4*, 407–413.

(22) Alonso, L.; Arce, A.; Francisco, M.; Soto, A. Thiophene separation from aliphatic hydrocarbons using the 1-ethyl-3-methylimidazolium ethylsulfate ionic liquid. *Fluid Phase Equilib.* **2008**, *270*, 97–102.

(23) Domañska, U.; Laskowska, M. Phase equilibria and volumetric properties of (1-ethyl-3-methylimidazolium ethylsulfate + alcohol or water) binary systems. *J. Solution Chem.* **2008**, *37*, 1271–1287.

(24) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; Willey: New York, 1986.

(25) Spiteri, W. L.; Letcher, T. M. The excess enthalpies of cyclooctane+n-alkanes. *Thermochim. Acta* **1982**, *59*, 73–80.

(26) Watson, E. P.; McLure, I. A.; Bennett, J. E.; Benson, G. C. Excess Properties of Some Aromatic-Alicyclic Systems. I. Measurements of Enthalpies and Volumes of Mixing. *J. Phys. Chem.* **1965**, *69*, 2753–2758.

(27) González, B.; Domínguez, I.; González, E. J.; Domínguez, A. Density, speed of sound, and refractive index of the binary systems cyclohexane (1) or methylcyclohexane (1) or cyclo-octane (1) with benzene (2), toluene (2), and ethylbenzene (2) at two temperatures. *J. Chem. Eng. Data* **2010**, *55*, 1003–1011.

(28) Arce, A.; Earle, M. J.; Rodríguez, H.; Seddon, K. R. Separation of aromatic hydrocarbons from alkanes using the ionic liquid 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide. *Green Chem.* **2007**, *9*, 70–74.

(29) Domanska, U.; Pobudkowska, A.; Królikowski, M. Separation of aromatic hydrocarbons from alkanes using ammonium ionic liquid C_2NTf_2 at $T = 298.15$ K. *Fluid Phase Equilib.* **2007**, *259*, 173–179.

(30) González, E. J.; Calvar, N.; González, B.; Domínguez, A. (Liquid + liquid) equilibria for ternary mixtures of (alkane + benzene + [EMpy] [ESO_4]) at several temperatures and atmospheric pressure. *J. Chem. Thermodyn.* **2009**, *41*, 1215–1221.

(31) Chen, J.; Li, Z.; Duan, L. Liquid-liquid equilibria of ternary and quaternary systems including cyclohexane, 1-heptene, benzene, toluene, and sulfolane at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 689–692.

(32) Sorensen, J. M.; Alt, W. *Liquid-liquid equilibrium data collection*; DECHEMA Chemistry Data Series: Frankfurt, 1980.

(33) Kato, R.; Krummen, M.; Gmehling, J. Measurement and correlation of vapor-liquid equilibria and excess enthalpies of binary systems containing ionic liquids and hydrocarbons. *Fluid Phase Equilib.* **2004**, *224*, 47–54.

Received for review May 14, 2010. Accepted July 30, 2010. The authors are grateful to the Ministerio de Ciencia e Innovación (Spain) for the financial support of the project CTQ2007-61272. Begoña González is also grateful to the Ministerio de Ciencia e Innovación (Spain) for financial support via the Ramón y Cajal Programme (RYC-2008-02388).

JE100508Y