Separation of Benzene from Linear Alkanes (C_6-C_9) Using 1-Ethyl-3-Methylimidazolium Ethylsulfate at $T = 298.15$ K

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In this work, the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate, [EMim][ESO_4], is used to separate benzene from alkanes (hexane, heptane, octane, nonane) by solvent extraction through the study of the liquid−liquid equilibria of the ternary systems at $T = 298.15$ K and atmospheric pressure. The selectivity, solute distribution ratio, and percent removal of the aromatic, calculated from the tie-line data, were used to determine whether this ionic liquid is a good solvent for the extraction of benzene from alkane compounds. The consistency of the tie-line data was ascertained by applying the Othmer−Tobias equation, and the experimental results for the ternary systems were correlated with the nonrandom two-liquid (NRTL) and the universal quasi-chemical (UNIQUAC) models.

Introduction

The separation of aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes) from C_4-C_{10} aliphatic hydrocarbon mixtures is challenging since these compounds have boiling points in a close range and several combinations form azeotropes. Liquid−liquid extraction can be a useful separation process, reducing the energy consumption and the environmental impact. Liquid−liquid equilibrium (LLE) data provide important information in developing processes for the separation of desired products from mixtures of hydrocarbons, and its use in chemical engineering is fundamental to wide industrial applications. Experimental LLE data are also required for checking the potential of thermodynamic models and for understanding the thermodynamic behavior present in these mixtures.

In the last years, there has been an increase in publications concerning the extraction of aromatic hydrocarbons from mixtures of aromatic and aliphatic hydrocarbons using ionic liquids.[1–8] These works are useful for the study of the influence of the structure of the ionic liquid on these separations.

The aim of this work is to investigate the possibility of using an imidazolium-based ionic liquid as a solvent in separating benzene from hexane, heptane, octane, and nonane. Therefore, liquid−liquid equilibria data for the ternary mixtures alkane + benzene + 1-ethyl-3-methylimidazolium ethylsulfate, [EMim][ESO_4], were determined. From the experimental data, the percent removal of the aromatic, the selectivity, and solute distribution ratio were calculated to determine the possibility of separating benzene from alkanes using a liquid extraction process. The consistency of experimental data was ascertained by applying the Othmer−Tobias equation.[9] The nonrandom two-liquid (NRTL)[10] and universal quasi-chemical (UNIQUAC)[11] models were used to correlate the experimental data for the studied ternary systems.

Experimental Section

Chemicals. Hexane, nonane, and benzene were supplied by Sigma-Aldrich with purities higher than 0.990, 0.990, and 0.999 mass fraction, respectively, and heptane and octane were purchased from Fluka with purity higher than 0.995 mass fraction. They were degassed ultrasonically and dried over molecular sieves type 4 Å, supplied by Aldrich, and kept in an inert argon atmosphere.

The ionic liquid used in this work was synthesized in the laboratory using standard procedures for other sulfate ionic liquids.[12] Typical synthesis and purification procedures have been published in a previous work.[13] It was purified by heating in a vacuum (0.2 Pa, 343.15 K) for several days to remove possible traces of other solvents and moisture. The water content was determined using a 787 Karl Fischer Titrino, and the ionic liquid showed that the mass fraction of water was less than $6 \cdot 10^{-4}$. To ensure its purity, the final product was checked by nuclear magnetic resonance (NMR) spectroscopy. The purity of 1-ethyl-3-methylimidazolium ethylsulfate, [EMim][ESO_4] (MW = 236.29 $g \cdot mol^{-1}$), is higher than 0.99 in mass fraction. The ionic liquid was kept in bottles with inert gas.

Apparatus and Procedure. An Anton Paar DSA-5000 digital vibrating tube densimeter with an uncertainty of $\pm 3 \cdot 10^{-5}$ $g \cdot cm^{-3}$ was used in this work for the measurements of density of the pure liquids and mixtures. The measurement of refractive indices of pure components was carried out with an automatic refractometer (Abbemat-HP, Dr. Kernchen) with an uncertainty in the experimental measurements of $\pm 4 \cdot 10^{-5}$. 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 the temperature of mixtures was maintained constant in a thermostatic bath (PoliScience digital temperature controller) with a precision of ± 0.01 K.

The binodal curves for the ternary systems at $T = 298.15$ K were determined using the cloud-point method by titrating binary mixtures of known compositions with the third component until the transition was visually determined. The density of each sample was measured, and a polynomial expression for the

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

alkane-rich phase		ionic liquid-rich phase				
x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}	% removal of aromatic	β	S
Hexane (1) + Benzene (2) + [EMim][ESO$_4$] (3)						
0.949	0.051	0.013	0.031	17.1	0.61	44.37
0.890	0.110	0.011	0.066	18.8	0.60	48.55
0.833	0.167	0.010	0.097	17.7	0.58	48.38
0.774	0.226	0.009	0.128	17.3	0.57	48.71
0.657	0.343	0.008	0.184	17.3	0.54	44.06
0.530	0.470	0.007	0.238	17.4	0.51	38.34
0.398	0.602	0.006	0.290	15.1	0.48	31.95
0.280	0.720	0.005	0.336	18.5	0.47	26.13
Heptane (1) + Benzene (2) + [EMim][ESO$_4$] (3)						
0.944	0.056	0.007	0.031	18.9	0.55	74.65
0.890	0.110	0.007	0.062	17.3	0.56	71.66
0.834	0.166	0.007	0.097	18.4	0.58	69.62
0.773	0.227	0.007	0.124	17.8	0.55	60.32
0.659	0.341	0.006	0.178	17.2	0.52	57.33
0.538	0.462	0.006	0.232	17.3	0.50	45.03
0.415	0.585	0.006	0.280	17.6	0.48	33.11
0.284	0.716	0.006	0.330	17.7	0.46	21.82
Octane (1) + Benzene (2) + [EMim][ESO$_4$] (3)						
0.934	0.066	0.003	0.033	20.4	0.52	155.67
0.884	0.116	0.003	0.060	17.7	0.53	152.41
0.825	0.175	0.003	0.090	18.1	0.52	141.43
0.765	0.235	0.002	0.109	17.9	0.47	118.28
0.655	0.345	0.003	0.173	17.2	0.50	109.48
0.527	0.473	0.003	0.229	17.5	0.48	85.05
0.409	0.591	0.003	0.277	17.5	0.47	63.90
0.275	0.725	0.002	0.331	17.9	0.46	62.78
0.139	0.861	0.001	0.387	18.5	0.45	62.48
Nonane (1) + Benzene (2) + [EMim][ESO$_4$] (3)						
0.948	0.052	0.002	0.028	16.8	0.54	255.23
0.885	0.115	0.002	0.059	18.5	0.51	227.02
0.825	0.175	0.002	0.089	18.1	0.51	209.79
0.771	0.229	0.002	0.118	18.4	0.52	198.64
0.647	0.353	0.002	0.175	16.9	0.50	160.38
0.525	0.475	0.002	0.231	18.8	0.49	127.66
0.403	0.597	0.002	0.278	18.0	0.47	93.83
0.277	0.723	0.002	0.331	18.1	0.46	63.41
0.147	0.853	0.001	0.385	19.3	0.45	66.35

density as a function of composition was obtained. In Table S1, available in Supporting Information, compositions of the binodal curves together with their density and polynomial expressions are summarized. It is important to mention that since the ionic liquid is immiscible with the binary systems alkane (1) + benzene (2), the presence of ionic liquid in the alkane-rich phase was assumed to be zero, and the binodal curve in this zone was obtained from the density versus mole fraction of the binary systems alkane (1) + benzene (2), previously published.[14]

Three validation points for each ternary system were evaluated to estimate the error of the technique used for the determination of the binodal curves, and they were chosen to cover the whole range of the binodal curves. These points were obtained by weighing, and then their densities were determined. The compositions of these points were calculated through the above-mentioned polynomial expression, and the obtained values were compared with the experimental compositions, as summarized in Table S2, available in SI. The maximum error was estimated to be ± 0.007 in mole fraction.

For the tie-line determination, mixtures with compositions inside the immiscible region were introduced into glass cells, stirred, and then left overnight to settle down. A sample from each phase was withdrawn using a syringe, and their densities were determined. The calculation of the tie-line compositions was carried out using the above-mentioned polynomial expressions and the values of the density versus mole fraction for the binary systems alkane (1) + benzene (2), and they are presented in Table 1.

Results and Discussion

The liquid−liquid equilibria for the ternary systems alkane (hexane, heptane, octane, or nonane) (1) + benzene (2) + [EMim][ESO$_4$] (3) were carried out at T = 298.15 K and atmospheric pressure. The experimental tie-lines are reported in Table 1 along with the percent removal of the aromatic, solute distribution ratio, β, and selectivity, S, and Figure 1 shows the triangular diagrams for the four studied systems. After inspection of the experimental data, it can be deduced that an increase in the chain length of the alkane, that is, from hexane to nonane, leads to an increase in the size of the immiscibility region. This behavior is in accordance with previous works on LLE of systems containing an alkane + aromatic + IL.[15,16]

The percent removal of the aromatic was expressed as 100 × (the amount of benzene extracted by the ionic liquid divided by the total amount of benzene extracted in the two phases). The solute distribution ratio, β, and the selectivity, S, are parameters that are generally used to characterize the suitability of a solvent for liquid extraction. They can be calculated from the experimental composition of the tie-line ends:

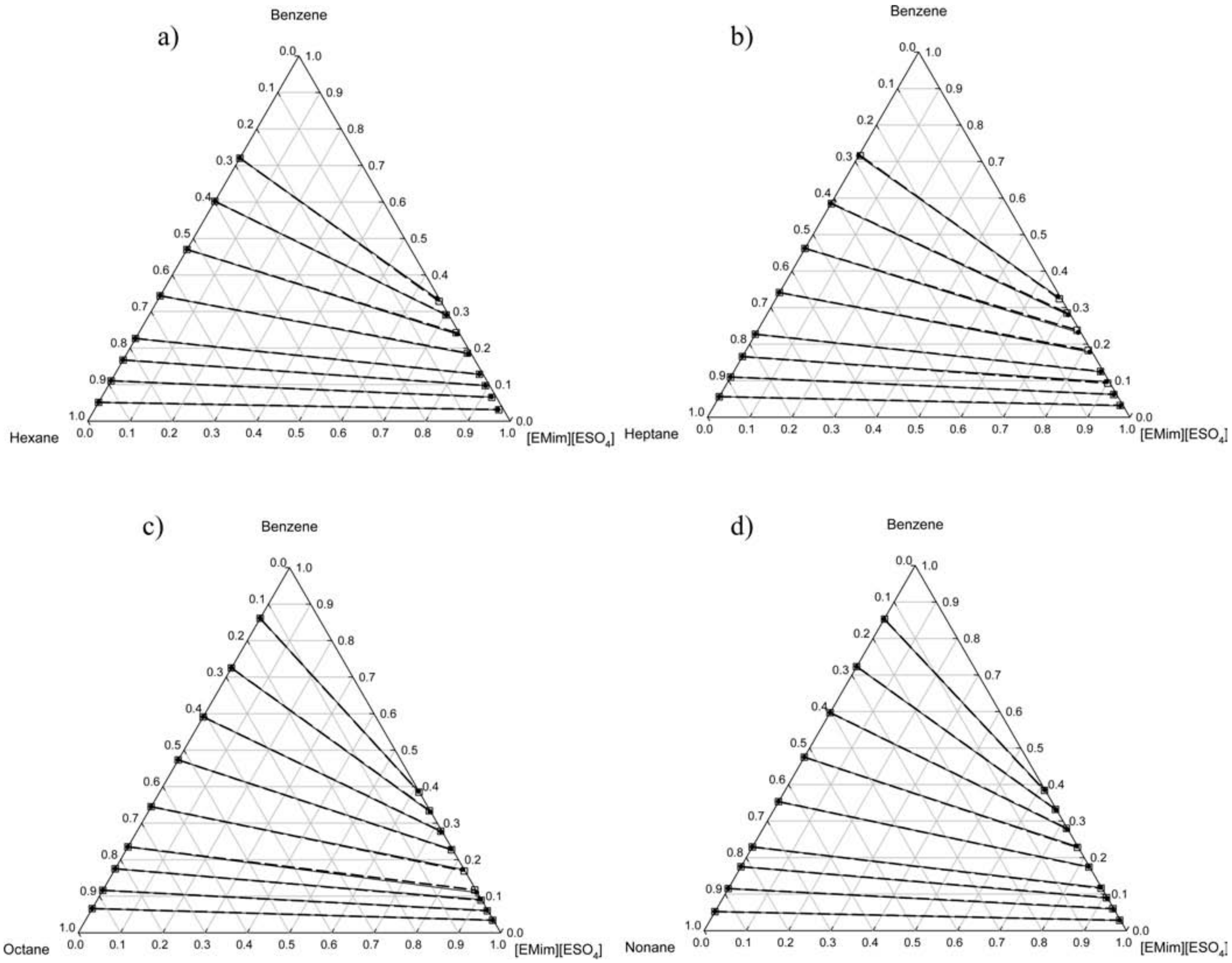

Figure 1. LLE of the ternary systems alkane (1) + benzene (2) + [EMim][ESO$_4$] (3): (a) hexane, (b) heptane, (c) octane, and (d) nonane, at $T = 298.15$ K. Solid lines and full points indicate experimental tie-lines, and dashed lines and empty squares indicate calculated data from the NRTL model.

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

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

where x_1^{I} and x_2^{I} are the mole fractions of alkane and benzene, respectively, in the alkane-rich phase, and x_1^{II} and x_2^{II} are the mole fractions of alkane and benzene, respectively, in the IL-rich phase.

The selectivities of the studied ternary systems are plotted in Figure 2. For the ternary systems studied in this work, the selectivity decreases as the benzene concentration in the raffinate phase increases as it was observed in several published data.[3,17–22] It has been published[6,23] that the aromatic solutes and the ionic liquid cations interact in an alternating structure though $\pi-\pi$ interactions with ionic liquid anions. As the aromatic content increases, the distance between aromatic solutes and cations becomes larger, and therefore the strength of interaction and, consequently, the solute distribution ratio are reduced. It is also remarkable that the selectivity values increase as the alkane chain increases, in the form hexane < heptane < octane < nonane, following the trend of the size of the immiscible region. The selectivity values are higher than unity for all of the studied systems, confirming that this ionic liquid can be a choice for extraction processes, although the solute distribution ratio values should be also considered, since β is

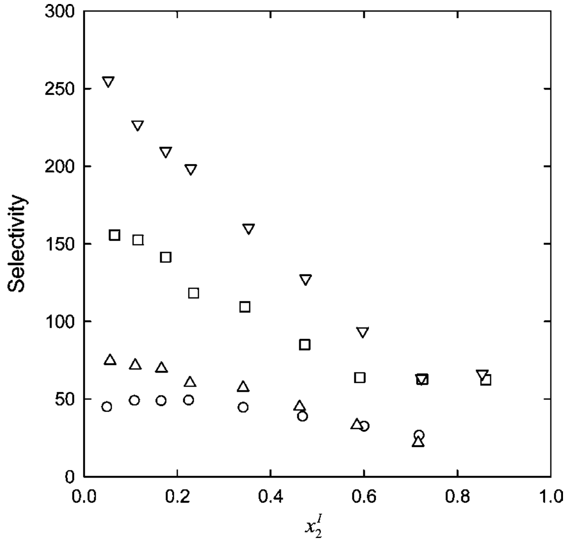

Figure 2. Selectivity of benzene for the ternary systems alkane (1) + benzene (2) + [EMim][ESO$_4$] (3): ○, hexane; △, heptane; □, octane; ▽, nonane; at $T = 298.15$ K.

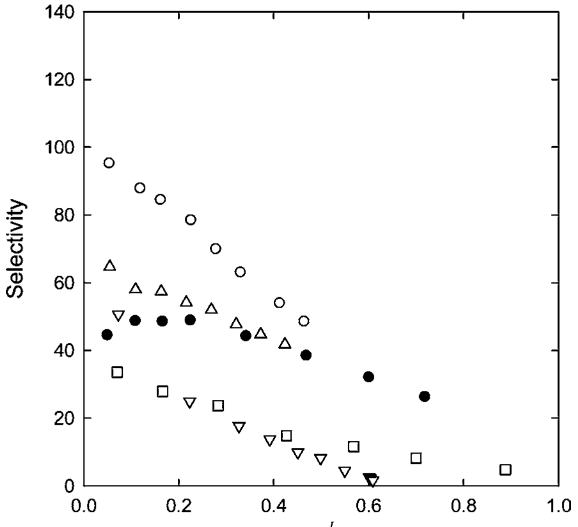

Figure 3. Selectivity of benzene for the ternary system hexane (1) + benzene (2) + solvent (3) at $T = 298.15$ K: ○, [EMim][ESO$_4$] as solvent (from ref 24); △, [BMim][MSO$_4$] as solvent (from ref 8); ●, [EMim][ESO$_4$] as solvent (from this work); □, [EMim][NTf$_2$] as solvent (from ref 3); ▽, sulfolane as solvent (from ref 25).

lower than unity and this implies more complex processes and more quantities of ionic liquid. However, as the IL can be recovered, the main costs are the initial concern. The values of the percent removal of the aromatic are similar for the four studied systems.

In Figure 3, experimental and literature selectivities for the ternary system hexane (1) + benzene (2) + solvent (3) are compared.[3,8,24,25] As can be observed in this figure, the use of 1-butyl-3-methylimidazolium methylsulfate, [BMim][MSO$_4$], and 1-ethyl-3-methylimidazolium ethylsulfate, [EMim][ESO$_4$], leads to selectivity values higher than sulfolane. The literature values for the system hexane (1) + benzene (2) + [EMim][ESO$_4$] (3) are higher than those obtained in this work. Nevertheless, considering the type of ternary diagrams, and that the small variation in the compositions has a great effect on selectivity, this parameter should be interpreted as a range, and the compared values could be considered in the same order. In case of the literature LLE data of the ternary systems containing ionic liquids, the β values decrease as the benzene concentration in the raffinate phase increases; using sulfolane as solvent, the behavior of the β values is the opposite. The compared β values are in the same order, except for those obtained with the 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide, that are higher.

The experimental tie-line compositions can be ascertained by applying the equation provided by Othmer−Tobias:[9]

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

where w_1^{I} and w_2^{I} are the mass fraction of alkane and benzene, respectively, in the alkane-rich phase; w_2^{II} and w_3^{II} are the mass fraction of benzene and ionic liquid, respectively, in the IL-rich phase; and *a* and *b* are adjustable parameters. The linearity of these fittings indicates the degree of consistency of the experimental data. In Table S3, available in SI, the parameters obtained in the fitting of the experimental data using the Othmer−Tobias equation, together with their correlation factor, R^2, and the standard deviation, σ, for the studied ternary systems, are shown. As can be deduced from the correlation factors and the standard deviations presented in this table, the obtained experimental data are consistent.

Table 2. Structural Parameters for the UNIQUAC Equation

component	r_i	q_i
hexane[a]	4.500	3.856
heptane[a]	5.174	4.396
octane[a]	5.849	4.936
nonane[a]	6.523	5.476
benzene[a]	3.188	2.400
[EMim][ESO$_4$][b,c]	7.94	7.21

[a] From ref 26. [b] From ref 27. [c] From ref 28.

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

$i-j$	Δg_{ij}/kJ·mol^{-1}	Δg_{ji}/kJ·mol^{-1}	α_{ij}	σx	$\Delta\beta$
Hexane (1) + Benzene (2) + [EMim][ESO$_4$] (3)					
1−2	−5.756	9.932	0.11	0.158	1.271
1−3	62.399	7.189			
2−3	19.202	−6.341			
Heptane (1) + Benzene (2) + [EMim][ESO$_4$] (3)					
1−2	−3.947	8.409	0.12	0.180	2.346
1−3	48.032	7.697			
2−3	12.241	−3.698			
Octane (1) + Benzene (2) + [EMim][ESO$_4$] (3)					
1−2	−6.447	6.219	0.10	0.170	2.815
1−3	1609.750	14.833			
2−3	28.488	−9.053			
Nonane (1) + Benzene (2) + [EMim][ESO$_4$] (3)					
1−2	−4.739	5.883	0.15	0.067	1.038
1−3	17.739	7.652			
2−3	21.760	−4.926			

Thermodynamic Correlation. The experimental data obtained in this work were also used to test the capability of the NRTL[10] and UNIQUAC[11] models to describe the behavior of LLE of ternary systems containing ionic liquids. Following a common procedure, the nonrandomness parameter in the NRTL equation, α, was set to different values between 0 and 0.5 during calculations. The required van der Waals parameters, r_{i} and q_{i}, of the UNIQUAC model was taken from literature,[26–28] and they are presented in Table 2.

The fitting parameters of the correlation models, together with the values of the root-mean-square deviation of the composition, σx, and the mean error of the solute distribution ratio, $\Delta\beta$, are listed in Table 3, for the NRTL model, and Table 4 for the UNIQUAC model. These deviations give an idea of the quality of the correlation, and they were calculated as follows:

$$\sigma x = 100\sqrt{\frac{\sum_{i}^{M}\sum_{j}^{N-1}[(x_{ij}^{\mathrm{I,exp}} - x_{ij}^{\mathrm{I,calc}})^2 + (x_{ij}^{\mathrm{II,exp}} - x_{ij}^{\mathrm{II,calc}})^2]}{2MN}} \qquad (4)$$

$$\Delta\beta = 100\sqrt{\frac{1}{M}\sum_{k=1}^{M}\left(\frac{\beta_k - \beta_k^{\mathrm{calc}}}{\beta_k}\right)^2} \qquad (5)$$

where *M* is the number of tie-lines and *N* the number of components in the mixture.

After the inspection of the values of σx and $\Delta\beta$ presented in Tables 3 and 4 it can be inferred that the NRTL model gives slightly lower deviations for all systems except for the system containing heptane, although both models fit satisfactorily the

Table 4. Values of the UNIQUAC Binary Interaction Parameters and 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} $\text{kJ}\cdot\text{mol}^{-1}$	σx	$\Delta\beta$
Hexane (1) + Benzene (2) + [EMim][ESO_4] (3)				
1−2	−1.241	2.640	0.193	2.170
1−3	71.850	0.459		
2−3	11.121	−1.393		
Heptane (1) + Benzene (2) + [EMim][ESO_4] (3)				
1−2	−0.143	1.016	0.151	2.338
1−3	175.494	0.352		
2−3	0.898	0.602		
Octane (1) + Benzene (2) + [EMim][ESO_4] (3)				
1−2	0.732	−0.118	0.220	4.106
1−3	175.494	0.438		
2−3	0.630	0.724		
Nonane (1) + Benzene (2) + [EMim][ESO_4] (3)				
1−2	1.961	−1.198	0.356	2.975
1−3	5.446	0.609		
2−3	2.800	−0.692		

experimental data. It is remarkable that sometimes these models have problems to correlate the absence of ionic liquid in the alkane-rich phase, although, despite this, the results of the correlation are satisfactory.

As an example of the obtained correlation, in Figure 1 the experimental tie-lines and those obtained from the correlation with the NRTL model are plotted, and the goodness of the correlation can be visually confirmed.

Conclusions

LLE data were obtained for the ternary mixtures of hexane (1), heptane (1), octane (1), or nonane (1) + benzene (2) + [EMim][ESO_4] (3) at $T = 298.15$ K and atmospheric pressure, and the selectivity, solute distribution ratio, and percent removal of the aromatic were determined. The selectivity decreases as the benzene concentration in the alkane-rich layer increases, and it increases as the alkane chain increases. The selectivity values confirm this ionic liquid as a choice for extraction processes, although the solute distribution ratios are lower than unity, implying a high quantity of ionic liquid needed. Nevertheless, the easiness of the recovery and reuse of the ionic liquid must be considered as a great advantage.

The consistency of the tie-lines was ascertained by means of the Othmer−Tobias equation, and the experimental data of LLE were satisfactorily correlated by the NRTL and UNIQUAC models, showing that both models are appropriate for systems containing ionic liquids.

Supporting Information Available:

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

Literature Cited

(1) 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.

(2) Arce, A.; Earle, M. J.; Rodríguez, H.; Seddon, K. R. Separation of benzene and hexane by solvent extraction with 1-alkyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide ionic liquids: Effect of the alkyl-substituent length. *J. Phys. Chem. B* **2007**, *111*, 4732–4736.

(3) 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.

(4) 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.

(5) Meindersma, G. W.; Podt, A.; de 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.

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

(7) Hansmeier, A. R.; Minoves, M.; Meindersma, G. W.; de Haan, A. B. Liquid-liquid equilibria for the three ternary systems (3-methyl-*N*-butylpyridinium dicyanamide + toluene + heptane), (1-butyl-3-methylimidazolium dicyanamide + toluene + heptane) and (1-butyl-3-methylimidazolium thiocyanate + toluene + heptane) at $T = (313.15 \text{ and } 348.15)$ K and $p = 0.1$ MPa. *J. Chem. Eng. Data* **2010**, *55*, 708–713.

(8) García, J.; Fernández, A.; Torrecilla, J. S.; Oliet, M.; Rodríguez, F. Ternary liquid-liquid equilibria measurement for hexane and benzene with the ionic liquid 1-butyl-3-methylimidazolium methylsulfate at $T = (298.2, 313.2, \text{ and } 328.2)$ K. *J. Chem. Eng. Data* **2010**, *55*, 258–261.

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

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

(11) 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.

(12) 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.

(13) Gómez, E.; González, B.; Calvar, N.; Tojo, E.; Domínguez, A. Physical properties of pure 1-ethyl-3-methylimidazolium ethylsulfate and its binary mixtures with ethanol and water at several temperatures. *J. Chem. Eng. Data* **2006**, *51*, 2096–2102.

(14) González, B.; González, E. J.; Domínguez, I.; Domínguez, A. Excess properties of binary mixtures hexane, heptane, octane and nonane with benzene, toluene and ethylbenzene at $T = 288.15$ and 298.15 K. *Phys. Chem Liq.* **2010**; DOI: 10.1080/00319100903164499.

(15) 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.

(16) González, E. J.; Calvar, N.; Gómez, E.; Domínguez, A. Separation of benzene from alkanes using 1-ethyl-3-methylpyridinium ethylsulfate ionic liquid at several temperatures and atmospheric pressure: Effect of the size of the aliphatic hydrocarbons. *J. Chem. Thermodyn.* **2010**, *42*, 104–109.

(17) 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.

(18) 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.

(19) Letcher, T. M.; Deenadayalu, N. Ternary liquid-liquid equilibria for mixtures of 1-methyl-3-octyl-imidazolium chloride + benzene + an alkane at $T = 298.2$ K and 1 atm. *J. Chem. Thermodyn.* **2003**, *35*, 67–76.

(20) Meindersma, G. W.; Podt, A.; de Haan, A. B. Selection of ionic liquids for the extraction of aromatic hydrocarbons from aromatic/aliphatic mixtures. *Fuel Process. Technol.* **2005**, *87*, 59–70.

(21) Zhang, J.; Huang, C.; Chen, B.; Ren, P.; Lei, Z. Extraction of aromatic hydrocarbons from aromatic/aliphatic mixtures using chloroaluminate room-temperature ionic liquids as extractants. *Energy Fuels* **2007**, *21*, 1724–1730.

(22) Zhu, J.; Chen, J.; Li, C.; Fei, W. Centrifugal extraction for separation of ethylbenzene and octane using 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid as extractant. *Sep. Purif. Technol.* **2007**, *56*, 237–240.

(23) Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyzen, M.; Sheppard, O.; Hardacre, C.; Rogers, R. D. Liquid clathrate formation in ionic liquid-aromatic mixtures. *Chem. Commun.* **2003**, 476–477.

(24) García, J.; Fernández, A.; Torrecilla, J. S.; Oliet, M.; Rodríguez, F. Liquid-liquid equilibria for {hexane + benzene + 1-ethyl-3-methy-

limidazolium ethylsulfate} at (298.2, 313.2 and 328.2) K. *Fluid Phase Equilib.* **2009**, *282*, 117–120.

(25) Chen, J.; Duan, L. P.; Mi, J. G.; Fei, W. Y.; Li, Z. C. Liquid-liquid equilibria of multi-component systems including n-hexane, n-octane, benzene, toluene, xylene and sulfolane at 298.15 K and atmospheric pressure. *Fluid Phase Equilib.* **2000**, *173*, 109–119.

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

(27) 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.

(28) 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.

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