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Liquid−Liquid Equilibrium for Ternary Mixtures of Hexane + Aromatic Compounds + [EMpy][ESO$_4$] at $T = 298.15$ K[†]

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Liquid−liquid equilibrium (LLE) data for the ternary systems hexane + toluene + 1-ethyl-3-methylpyridinium ethylsulfate and hexane + ethylbenzene + 1-ethyl-3-methylpyridinium ethylsulfate were measured at $T = 298.15$ K and atmospheric pressure. Selectivity and solute distribution ratio, derived from the equilibrium data, were used to determine if this ionic liquid can be used as a potential extracting solvent for the separation of aromatic compounds from hexane. The consistency of tie-line data was ascertained by applying the Othmer−Tobias and Hand equations. The experimental data for the ternary systems were well correlated with the nonrandom two-liquid (NRTL) equation. The results were compared to those previously published for the separation of benzene from hexane using the same ionic liquid, therefore analyzing the influence of the radical in the benzene ring.

Introduction

The separation of aromatic hydrocarbons (e.g., benzene, toluene, and ethylbenzene) from aliphatic compounds is of great importance for the petrochemical industry for two basic reasons: the first is to meet the high demand of aromatic compounds by chemical industry, and the second reason is 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,[2−5] *N*-formylmorpholine,[6] *N*-methylimidazole or *N*-ethylimidazole,[7] glycols,[8−10] propylene carbonate,[11] or combinations of solvents, are used for the extraction of aromatics. In separations, a distillation step is usually also necessary to separate the solvent used from extract and raffinate phases. Nevertheless, when the ionic liquids are used, the process is much simpler because no distillation step is necessary, and the recovery of the ionic liquid solvent is much easier.[12]

Nowadays, there are few publications concerning extraction of aromatic hydrocarbons from mixtures of aromatic and aliphatic hydrocarbons using ionic liquids.[13−23]

This work is a continuation of a study on the extraction of benzene from hexane and heptane using the ionic liquid 1-ethyl-3-methylpyridinium ethylsulfate, [EMpy][ESO$_4$].[23] As the results were good, the research was expanded to the separation of other aromatics (toluene and ethylbenzene) from hexane using the same ionic liquid.

The liquid−liquid equilibria (LLE) for the ternary systems hexane (1) + toluene (2) + 1-ethyl-3-methylpyridinium ethylsulfate (3) and hexane (1) + ethylbenzene (2) + 1-ethyl-3-methylpyridinium ethylsulfate (3) were determined at $T = 298.15$ K and atmospheric pressure. From experimental data, it was possible to calculate the selectivity and solute distribution ratio which are widely used parameters to characterize the suitability of a solvent in liquid extraction. The Othmer−Tobias and Hand equations were used to test the consistency of experimental data. These data were also correlated using the NRTL equation, to facilitate the implementation and use of the data in computerized applications.

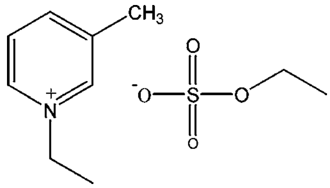

Figure 1. Structure of the ionic liquid 1-ethyl-3-methylpyridinium ethylsulfate [EMpy][ESO$_4$].

Experimental Section

Chemicals. Hexane, toluene, and ethylbenzene were supplied by Sigma-Aldrich with purity higher than 99.0 %, 99.9 %, and 99.8 % in mass fraction, respectively. 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.[24] Typical synthesis and purification procedures have been published in a previous work.[25] To ensure its purity, a NMR was made. The purity of 1-ethyl-3-methylpyridiniym ethylsulfate, [EMpy][ESO$_4$] (MW $= 247.32$ g·mol^{-1}), is higher than 99 % in mass fraction. The structure of this ionic liquid is presented in Figure 1.

The ionic liquid was kept in bottles with inert gas. Before using, the sample was subjected to vacuum ($P = 0.2$ Pa) and moderate temperature ($T = 323.15$ 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 ionic liquid showed that the mass fraction of water was less than $7 \cdot 10^{-4}$.

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

	$\rho/(g \cdot cm^{-3})$		n_D	
component	exptl	lit.	exptl	lit.
hexane	0.65519	0.65484[a]	1.37234	1.37226[a]
toluene	0.86217	0.86219[a]	1.49399	1.49390[b]
ethylbenzene	0.86251	0.86253[a]	1.49304	1.49320[a]
[EMpy][ESO$_4$]	1.21961	1.22226[c]	1.50591	1.50666[c]

[a] From ref 26. [b] From ref 27. [c] From ref 25.

Table 2. Binodal Curves of Ternary Systems Hexane (1) + Aromatic Compound (2) + [EMpy][ESO$_4$] (3) at T = 298.15 K

x_1	x_2	$\rho/(g \cdot cm^{-3})$
Hexane (1) + Toluene (2) + [EMpy][ESO$_4$] (3)		
0.009	0.000	1.21717
0.016	0.026	1.21366
0.011	0.050	1.21076
0.016	0.099	1.20139
0.006	0.115	1.19976
0.006	0.149	1.19342
0.002	0.202	1.18476
0.003	0.217	1.18119
0.003	0.251	1.17373
0.000	0.307	1.16168
Hexane (1) + Ethylbenzene (2) + [EMpy][ESO$_4$] (3)		
0.009	0.000	1.21717
0.006	0.037	1.21146
0.005	0.058	1.20822
0.002	0.078	1.20513
0.001	0.121	1.19653
0.000	0.168	1.18588

The measured density and refractive index of the pure components at T = 298.15 K and their corresponding literature data[25−27] 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. LLE data for the studied systems were determined at T = 298.15 K. Binodal curves were obtained by the cloud point method,[28] while the tie-line compositions were determined by density measurements. The density of the pure liquids and mixtures was measured using an Anton Paar DSA-5000 digital vibrating tube densimeter with an uncertainty of ± $2.6 \cdot 10^{-5}$ $g \cdot cm^{-3}$. To measure refractive indices of pure components, an automatic refractometer (Abbemat-HP, Dr. Kernchen) with an uncertainty in the experimental measurements of ± $4 \cdot 10^{-5}$ was used.

The binodal curves of the studied systems were determined at T = 298.15 K and atmospheric pressure by titrating binary mixtures of known compositions with the third component until the transition was visually determined. These curves are presented in Table 2. For the preparation of samples, a Mettler AX-205 Delta Range balance with an uncertainty of ± $3 \cdot 10^{-4}$ g was used. The density of each sample was measured, and a polynomial expression for the density as a function of composition was obtained (and reported in Table 3).

Table 4. Density Data for Binary Systems of Hexane (1) + Aromatic Compound (2) at T = 298.15 K

x_1	$\rho/(g \cdot cm^{-3})$	x_1	$\rho/(g \cdot cm^{-3})$
Hexane (1) + Toluene (2)		Hexane (1) + Ethylbenzene (2)	
0.0000	0.86217	0.0000	0.86251
0.0830	0.84173	0.0903	0.84313
0.1713	0.82075	0.1776	0.82435
0.2980	0.79172	0.2675	0.80521
0.3960	0.77030	0.3777	0.78193
0.5011	0.74844	0.4931	0.75781
0.5949	0.72953	0.5929	0.73722
0.6973	0.70961	0.6947	0.71643
0.7961	0.69110	0.7984	0.69545
0.8946	0.67345	0.8942	0.67628
1.0000	0.65519	1.0000	0.65519

To estimate the error of the technique used for the determination of the binodal curves, three validation points were evaluated. 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 (using the Excel Solver), and the obtained values were compared with the experimental compositions. The maximum error was estimated to be ± 0.006 in mole fraction.

For the tie-line determination, mixtures with compositions inside the immiscible region were introduced into glass cells and closed using silicon covers. Special care was taken in covering the whole immiscibility region. The temperature was maintained constant in a thermostatic bath (PoliScience digital temperature controller) with a precision of ± 0.01 K. To guarantee the thermodynamic equilibrium, the 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 at the studied temperature to settle down. Then, a sample from each phase was withdrawn using a syringe to carry out the compositional analysis. The determination of the tie-line compositions for the ternary systems was carried out by correlating the densities of the two immiscible liquid phases of the conjugate solutions with the polynomial expressions of density versus composition. Note that since no ionic liquid was detected in the alkane-rich phase, the composition of this phase was determined using the density data versus molar fraction for the binary systems alkane (1) + aromatic (2), presented in Table 4. The tie-line compositions are summarized in Table 5.

Results and Discussion

The binodal curves for the ternary systems hexane (1) + aromatic compound (2) + [EMpy][ESO$_4$] (3) at T = 298.15 K are presented in Table 2. The validation points and the polynomial expression used for their determination are included in Table 3. The values of the density versus composition for

Table 3. Validation Points of Ternary Systems Hexane (1) + Aromatic Compound (2) + [EMpy][ESO$_4$] (3) at T = 298.15 K

x_1^{exptl}	x_2^{exptl}	$\rho^{exptl}/(g \cdot cm^{-3})$	x_1^{calc}	x_2^{calc}
Hexane (1) + Toluene (2) + [EMpy][ESO$_4$] (3)				
$\rho = 1.218457 - 0.089083x_1 - 0.247904x_1^2 - 0.001498x_1^3 - 0.138925x_2 - 0.147372x_2^2 - 0.006638x_2^3$				
0.009	0.071	1.20654	0.013	0.072
0.005	0.122	1.19847	0.009	0.122
0.002	0.199	1.18462	0.004	0.199
Hexane (1) + Ethylbenzene (2) + [EMpy][ESO$_4$] (3)				
$\rho = 1.218983 - 0.217892x_1 + 1.379059x_1^2 + 0.027438x_1^3 - 0.160493x_2 - 0.110594x_2^2 - 0.638294x_2^3$				
0.006	0.034	1.21299	0.006	0.029
0.003	0.061	1.20797	0.004	0.060
0.003	0.091	1.20239	0.002	0.092

Table 5. Experimental Liquid−Liquid Equilibrium Data in Mole Fraction for Ternary Systems of Hexane (1) + Aromatic Compound (2) + [EMpy][ESO$_4$] (3) at T = 298.15 K and Calculated 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}	β	S
Hexane (1) + Toluene (2) + [EMpy][ESO$_4$] (3)					
0.938	0.062	0.012	0.019	0.31	23.95
0.886	0.114	0.014	0.038	0.33	21.10
0.828	0.172	0.013	0.062	0.36	22.96
0.767	0.233	0.012	0.085	0.36	23.32
0.711	0.289	0.010	0.108	0.37	26.57
0.646	0.354	0.009	0.129	0.36	26.16
0.501	0.499	0.005	0.173	0.35	34.74
0.122	0.878	0.000	0.285	0.32	-
Hexane (1) + Ethylbenzene (2) + [EMpy][ESO$_4$] (3)					
0.918	0.082	0.008	0.010	0.12	13.99
0.863	0.137	0.007	0.017	0.12	15.30
0.803	0.197	0.007	0.029	0.15	16.89
0.738	0.262	0.006	0.043	0.16	20.19
0.664	0.336	0.005	0.058	0.17	22.92
0.458	0.542	0.003	0.098	0.18	27.60
0.343	0.657	0.002	0.116	0.18	30.28

the binary systems hexane (1) + toluene (2) and hexane (1) + ethylbenzene (2) at T = 298.15 K are given in Table 4.

The LLE data for the ternary systems hexane (1) + toluene (2) + [EMpy][ESO$_4$] (3) and hexane (1) + ethylbenzene (2) + [EMpy][ESO$_4$] (3) at T = 298.15 K are presented in Table 5. Samples from the hexane-rich phase were assumed as totally free of IL as was confirmed afterward by the ^{1}NMR analysis of some hydrocarbon-rich phases. Similar conclusions were obtained by other authors using other ionic liquids and other techniques.[15,20] The ternary phase diagrams of the studied systems along with the previously published[23] hexane (1) + benzene (2) + [EMpy][ESO$_4$] (3) system at T = 298.15 K are shown in Figure 2 for visual comparison. By inspection of this figure, it can be observed that benzene, toluene, and ethylbenzene present partial solubility in [EMpy][ESO$_4$] and that the alkane and aromatic compounds are completely soluble in all proportions. These ternary diagrams correspond to the Type 2 category, according to the classification proposed by Sorensen et al.,[29] with a wide immiscible zone, indicating that the solubility of the studied aromatic hydrocarbons in [EMpy][ESO$_4$] is much higher than that of hexane. The solubility of aromatic compounds in [EMpy][ESO$_4$] decreases in the order of benzene > toluene > ethylbenzene. The tie-lines cover almost all the triangular diagrams, which indicate that a good separation of the aromatic compound from hexane using [EMpy][ESO$_4$] ionic liquid is possible.

Together with the LLE experimental data, Table 5 includes the corresponding values for 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 hexane and aromatic compound, respectively, in the upper phase (alkane-rich phase) and x_1^{II} and x_2^{II} are the mole fractions of hexane and aromatic compound, respectively, in the lower phase (IL-rich phase). The variations of β with the composition of the aromatic compounds in the raffinate phase are plotted in Figure 3. The distribution coefficients of the aromatic compounds decrease with increasing compositions of the aromatic compound in the alkane-rich phase for the system hexane (1) + benzene (2) + [EMpy][ESO$_4$] (3) and increase slightly for the systems hexane (1) + toluene (2) + [EMpy][ESO$_4$] (3) and hexane (1) + ethylbenzene (2) + [EMpy][ESO$_4$] (3). Comparing the results of the three ternary systems, it can be seen that benzene presents higher solute distribution ratio than toluene or ethylbenzene. Similar results are published for other authors using different ionic liquids.[20,30]

The selectivity values are very similar in all the studied systems, and they show small variations with the concentration of aromatic compounds in the raffinate phase. The selectivity values for the studied systems are higher than unity, which confirms the extraction efficiency of this ionic liquid. 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 presence of radicals in the aromatic compound has a negative influence on the extraction, since S and β decrease, implying more stages and a higher quantity of ionic liquid.

The equations provided by Othmer−Tobias[31] and Hand[32] were used to ascertain the reliability of the experimental tie-line compositions

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

$$\ln\left(\frac{w_2^{\mathrm{I}}}{w_1^{\mathrm{I}}}\right) = c + d \ln\left(\frac{w_2^{\mathrm{II}}}{w_3^{\mathrm{II}}}\right) \tag{4}$$

where w_1^{I} and w_2^{I} are the mass fraction of hexane and aromatic, respectively, in the alkane-rich phase; w_2^{II} and w_3^{II} are the mass fraction of aromatic and ionic liquid, respectively, in the ionic liquid-rich phase; and a, b, c, and d are adjustable parameters. The linearity of these fittings indicates the degree of consistency of the experimental data. The Othmer−Tobias plots for the studied systems are shown in Figure 4, and the parameters obtained from the proposed equations are presented in Table 6, together with the correlation factor, R^2, for both systems at the studied temperature. As can be inferred from the R^2 values presented in this table, the Othmer−Tobias equation gives slightly better results than the Hand equation. It is important to mention that the higher deviations from linearity are obtained for the experimental tie-lines that present lower concentration of hexane, when the tie-line end is closer to the binary system.

Thermodynamic Correlation. The excess Gibbs energy model of NRTL[33] was employed to correlate the experimental liquid−liquid equilibrium data. This model was not originally intended for systems that involve electrolytes, but nevertheless it has been widely used in modeling both LLE and vapor−liquid equilibria (VLE) in a variety of electrolyte systems, usually leading to good correlations for systems containing ILs.[34]

In this model, the activity coefficients are calculated as follows

$$\ln \gamma_i = \left(\frac{\sum_{j=1}^{n} \tau_{ji} x_j G_{ji}}{\sum_{k=1}^{n} x_k G_{ki}}\right) + \sum_{j=1}^{n} \left(\frac{x_j G_{ij}}{\sum_{k=1}^{n} x_k G_{kj}}\right)\left(\tau_{ij} - \frac{\sum_{m=1}^{n} \tau_{mi} x_m G_{mi}}{\sum_{k=1}^{n} x_k G_{kj}}\right) \tag{5}$$

where

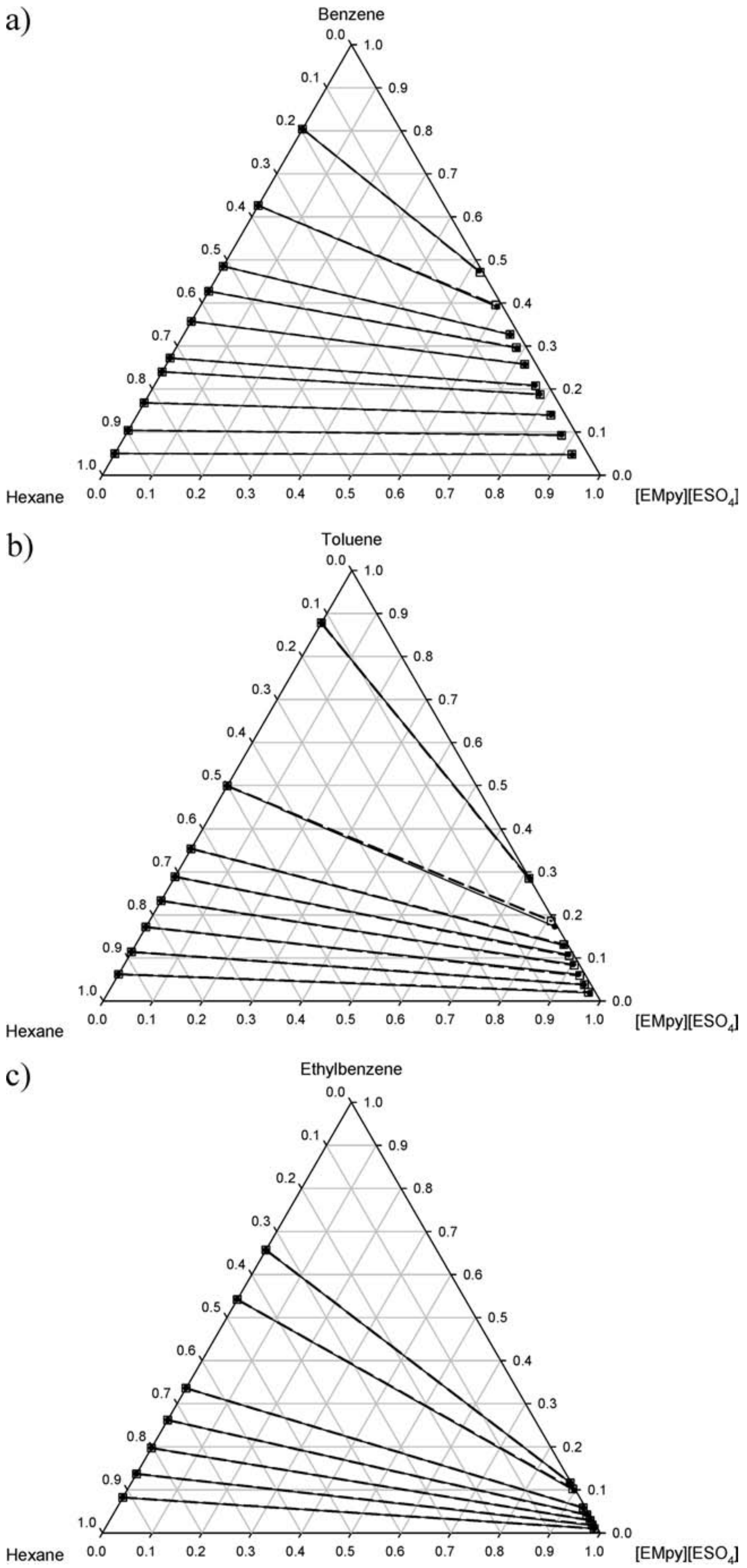

Figure 2. LLE of the ternary systems (a) hexane (1) + benzene (2) + [EMpy][ESO$_4$] (3) (from ref 23); (b) hexane (1) + toluene (2) + [EMpy][ESO$_4$] (3); and (c) hexane (1) + ethylbenzene (2) + [EMy][ESO$_4$] (3) at T = 298.15 K. Solid lines and full points indicate experimental tie-lines, and dashed lines and empty squares indicate calculated data from the NRTL model.

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} = \frac{\Delta g_{ij}}{RT} \qquad \tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{\Delta g_{ji}}{RT}$$

where x represents the mole fraction; g_{ij} is an energy parameter that characterizes the interaction of species i and j; R is the gas constant; T is the absolute temperature; and the parameter $\alpha_{ij} = \alpha_{ji}$ is related to the nonrandomness in the mixture. Although α_{ij} can be adjusted, in this case it will be considered fixed in a value of $\alpha_{ij} = 0.1$, which gave the best results after testing different values from $\alpha_{ij} = 0.1$ to 0.5. Treating the nonrandomnes parameter α_{ij} as an adjustable parameter leads to values that are far from the usual range, and no noticeable improvement is found for the correlation. The binary interaction parameters, Δg_{ij}, are estimated from experimental data. The objective function used minimizes the differences between the experimental and calculated mole fraction of the components in both phases.

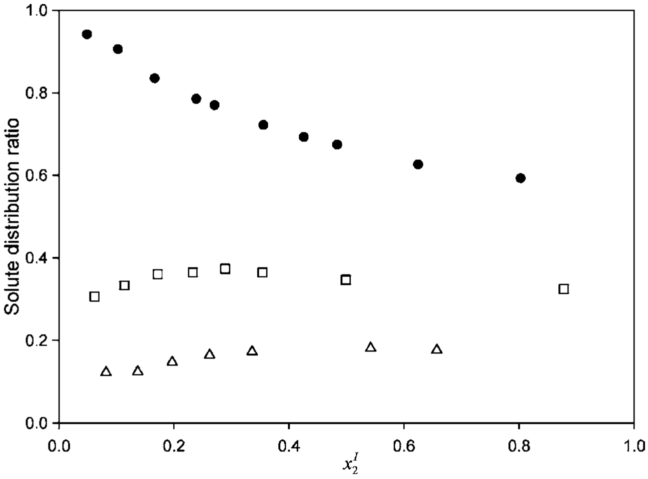

Figure 3. Solute distribution ratio for the ternary systems hexane (1) + aromatic compound (2) + [EMpy][ESO$_4$] (3), at T = 298.15 K, as a function of the mole fraction of aromatic compound in the alkane-rich phase. Aromatic compounds: ●, benzene (from ref 23); □, toluene; △, ethylbenzene.

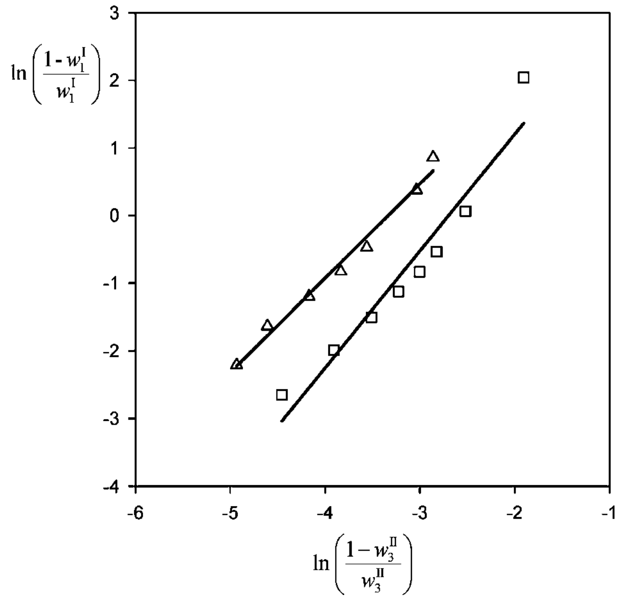

Figure 4. Othmer−Tobias plot for the systems □, hexane (1) + toluene (2) + [EMpy][ESO$_4$] (3); and △, hexane (1) + ethylbenzene (2) + [EMy][ESO$_4$] (3), at T = 298.15 K.

Table 6. Othmer−Tobias and Hand Equation Parameters, Together with the Correlation Factor, at T = 298.15 K for Both Ternary Systems

Othmer−Tobias equation		
a	b	R^2
Hexane (1) + Toluene (2) + [EMpy][ESO$_4$] (3)		
4.661	1.728	0.935
Hexane (1) + Ethylbenzene (2) + [EMpy][ESO$_4$] (3)		
4.646	1.393	0.985
Hand equation		
c	d	R^2
Hexane (1) + Toluene (2) + [EMpy][ESO$_4$] (3)		
3.955	1.435	0.909
Hexane (1) + Ethylbenzene (2) + [EMpy][ESO$_4$] (3)		
3.866	1.141	0.974

Table 7. NRTL Binary Interaction Parameters and Deviations for LLE Data of Ternary Systems with α = 0.1

$i-j$	Δg_{ij} (kJ·mol^{-1})	Δg_{ji} (kJ·mol^{-1})	σx	$\Delta\beta$
Hexane (1) + Toluene (2) + [EMpy][ESO$_4$] (3)				
1−2	−10.144	15.912	0.123	3.12
1−3	428.84	10.801		
2−3	39.991	−6.766		
Hexane (1) + Ethylbenzene (2) + [EMpy][ESO$_4$] (3)				
1−2	−9.336	23.368	0.071	2.85
1−3	173.238	11.917		
2−3	31.788	−3.311		

The NRTL binary interaction parameters of the ternary systems correlated are listed in Table 7, as well as the values of the root-mean-square deviation of the composition, σx, and the mean error of the solute distribution ratio, $\Delta\beta$. These deviations were calculated as follows

$$\sigma x = 100\sqrt{\frac{\sum_i^M \sum_j^{N-1} ((x_{ij}^{\mathrm{I,exptl}} - x_{ij}^{\mathrm{I,calc}})^2 + (x_{ij}^{\mathrm{II,exptl}} - x_{ij}^{\mathrm{II,calc}})^2)}{2MN}} \tag{6}$$

$$\Delta\beta = 100\sqrt{\frac{1}{M}\sum_k \left(\frac{\beta_k - \beta_k^{\mathrm{calc}}}{\beta_k}\right)^2} \tag{7}$$

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

The experimental LLE data are plotted in Figure 2 together with the correlation obtained with the NRTL model. As can be seen in Figure 2, the miscible region decreases as the alkyl chain of the aromatic compound increases in the form: benzene > toluene > ethylbenzene. As can be observed, ethylbenzene presents a lower solute distribution ratio than toluene, and toluene lower than benzene. The NRTL model used fits satisfactorily the experimental data, as shown in Figure 2 and Table 7, presenting small deviations. The nonrandomness parameter, α, was set to different values between 0.1 and 0.5 during calculations, and the correlation with α = 0.1 gave the best results in both cases.

Conclusions

The aim of this work is to obtain LLE data for the ternary systems hexane (1) + toluene (2) + [EMpy][ESO$_4$] (3) and hexane (1) + ethylbenzene (2) + [EMpy][ESO$_4$] (3) at T =

298.15 K. From the equilibrium data, the selectivity and solute distribution ratio are calculated. The selectivity range is similar for all studied systems, and the values are higher than unity. This indicates that [EMpy][ESO$_4$] is a potential solvent for the separation of aromatic compounds (benzene, toluene, and ethylbenzene) from hexane at $T = 298.15$ K. Benzene has a higher solute distribution ratio than toluene or ethylbenzene, requiring a lower solvent to feed ratio. The consistency of tie-line data is ascertained by applying the Othmer−Tobias and Hand equations, and the experimental LLE data can be satisfactorily correlated by the NRTL model.

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