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Effect of the Chain Length on the Aromatic Ring in the Separation of Aromatic Compounds from Methylcyclohexane Using the Ionic Liquid 1-Ethyl-3-methylpyridinium Ethylsulfate

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Liquid−liquid equilibrium (LLE) data for the ternary systems methylcyclohexane + benzene + 1-ethyl-3-methylpyridinium ethylsulfate, methylcyclohexane + toluene + 1-ethyl-3-methylpyridinium ethylsulfate, and methylcyclohexane + ethylbenzene + 1-ethyl-3-methylpyridinium ethylsulfate are reported under atmospheric pressure and at $T = 298.15$ K. The selectivity, the percent removal of aromatic compound, and the distribution coefficient were calculated from the LLE data, and the influence of the presence of radicals in the benzene ring were analyzed. The reliability of the experimental LLE data was ascertained using the Othmer−Tobias and Hand equations. The nonrandom two-liquid (NRTL) model was used to correlate the experimental data for the ternary systems. A search of the literature has indicated that data for the mixtures presented here have not been reported previously.

Introduction

Separations of aromatic compounds (e.g., benzene, toluene, and ethylbenzene) from aliphatic compounds are vitally important in the petrochemical industry for two principal reasons: first, for aromatic compound reduction or rather removal from fuel mixtures, and second, for the conditioning of naphtha streams.[1] The aromatic hydrocarbons are separated from naphtha using a typical liquid−liquid extraction process.[2,3]

In recent years, some authors have studied the application of different ionic liquids (ILs) for the extraction of aromatic compounds from alkanes by experimental measurements of the liquid−liquid equilibria (LLE).[4−14] Nevertheless, there are few publications concerning the extraction of aromatic hydrocarbons from mixtures of aromatic compound and cycloalkanes using ILs,[15,16] while for the studied systems data have not been found in the literature.

This work is a continuation of our investigation on ILs to study the possibility of using an IL as a solvent in separating aromatic compounds from aliphatic compounds. In previous papers,[17,18] the extraction of benzene from alkanes using the IL 1-ethyl-3-methylpyridinium ethylsulfate, [EMpy][ESO$_4$], as a solvent was tested. As the results were good, the research was expanded to the separation of aromatic hydrocarbons (benzene, toluene, and ethylbenzene) from a cycloalkane (methylcyclohexane).

In this work, the liquid−liquid equilibria (LLE) for the ternary systems methylcyclohexane (1) + benzene (2) + 1-ethyl-3-methylpyridinium ethylsulfate (3), methylcyclohexane (1) + toluene (2) + 1-ethyl-3-methylpyridinium ethylsulfate (3), and methylcyclohexane (1) + ethylbenzene (2) + 1-ethyl-3-methylpyridinium ethylsulfate (3) were determined at $T = 298.15$ K and atmospheric pressure. From the experimental data, the selectivity (S), the percent removal of aromatic compounds, and the distribution coefficient (β) were calculated to analyze the ability of this IL as solvent in liquid extraction processes.

The reliability of the experimentally measured LLE data was tested by the Othmer−Tobias[19] and Hand[20] equations. Finally, the LLE data have been correlated using the nonrandom two-liquid (NRTL) equation.[21]

Experimental Section

Chemicals. Methylcyclohexane, benzene, toluene, and ethylbenzene were supplied by Sigma-Aldrich with a mass fraction purity higher than 99.0 %, 99.9 %, 99.9 %, and 99.8 %, respectively. They were degassed ultrasonically and dried over type 4 Å molecular sieves, supplied by Aldrich, and kept in an inert argon atmosphere.

The IL used in this work was synthesized in our laboratory using standard procedures for other ILs that contain alkyl sulfate anions.[22] Typical synthesis and purification procedures have been published in a previous work.[23] To ensure its purity, ^{1}H NMR was done, and its density and refractive index were compared with literature values. The mass fraction purity of 1-ethyl-3-methylpyridinium ethylsulfate, [EMpy][ESO$_4$], is higher than 99 %.

The IL was kept in bottles with inert gas. Before using, the IL was treated by vacuum evaporation ($P = 0.2$ Pa) at a moderate temperature ($T = 323.15$ K) for several days to remove possible residual volatile impurities and moisture. The water content was determined using a 787 Karl Fischer Titrino, and the IL showed that the mass fraction of water was less than $7 \cdot 10^{-4}$.

The physical properties (density and refractive index) of the pure components and literature data[23−25] at $T = 298.15$ 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 literature samples.

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

	$\rho/(g \cdot cm^{-3})$		n_D	
component	exptl	lit.	exptl	lit.
[EMpy][ESO$_4$]	1.21961	1.22226[a]	1.50591	1.50666[a]
methylcyclohexane	0.76502	0.76506[b]	1.42062	1.42058[b]
benzene	0.87357	0.87360[b]	1.49774	1.49792[b]
toluene	0.86217	0.86219[b]	1.49399	1.49390[c]
ehtylbenzene	0.86251	0.86253[b]	1.49304	1.49320[b]

[a] From ref 23. [b] From ref 24. [c] From ref 25.

Apparatus and Procedure. LLE data for the studied systems were determined at $T = 298.15$ K. Binodal curves were obtained following a similar procedure to that described by Letcher et al.,[26] while the tie-line compositions were determined by density measurements. The density of the pure liquids and mixtures were measured using an Anton Paar DSA-5000 digital vibrating tube densimeter with an uncertainty of $\pm\ 3 \cdot 10^{-5}$ g·cm^{-3}. To measure refractive indices of pure components, an automatic refractometer (Abbemat-HP, Dr. Kernchen) with an uncertainty in the experimental measurements of $\pm\ 4 \cdot 10^{-5}$ 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. For the preparation of samples, a Mettler AX-205 Delta range balance with an uncertainty of $\pm\ 3 \cdot 10^{-4}$ g was used. The density of each sample was measured, and a polynomial expression for the density as function of composition was obtained.

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, and the obtained values were compared with the known compositions. The maximum uncertainty was estimated to be ± 0.007 in mole fraction.

For the tie-line determination, mixtures of known 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 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 tie-line compositions for the ternary systems were determined by correlating the densities of the two immiscible liquid phases of the conjugate solutions with the polynomial expressions of density versus composition. Since it was found that the IL is totally immiscible in the pure studied components (methylcyclohexane and aromatic compounds), the presence of the IL in the methylcyclohexane-rich phase was assumed to be zero, and the composition of this phase was determined using the values of density versus mole fraction for the binary systems of methylcyclohexane (1) + aromatic compound (2).

Results and Discussion

The compositions of the binodal curves for the ternary systems methylcyclohexane (1) + aromatic compound (2) + [EMpy][ESO$_4$] (3) at $T = 298.15$ K are given in Table 2. As part of the binodal curves, the values of the density versus composition for the binary systems methylcyclohexane (1) + benzene (2), methylcyclohexane (1) + toluene (2), and methylcyclohexane (1) + ethylbenzene (2) at $T = 298.15$ K were taken from literature.[27]

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

x_1	x_2	$\rho/(g \cdot cm^{-3})$
Methylcyclohexane (1) + Benzene (2) + [EMpy][ESO$_4$] (3)		
0.016	0.000	1.21632
0.010	0.049	1.21058
0.014	0.098	1.20298
0.008	0.151	1.19678
0.015	0.198	1.18801
0.007	0.246	1.18103
0.017	0.289	1.17181
0.001	0.385	1.15511
0.002	0.503	1.12599
0.002	0.529	1.12141
0.000	0.591	1.10484
Methylcyclohexane (1) + Toluene (2) + [EMpy][ESO$_4$] (3)		
0.016	0.000	1.21632
0.009	0.052	1.20917
0.012	0.101	1.20093
0.006	0.154	1.19178
0.003	0.206	1.18279
0.002	0.256	1.17322
0.000	0.307	1.16168
Methylcyclohexane (1) + Ethylbenzene (2) + [EMpy][ESO$_4$] (3)		
0.016	0.000	1.21632
0.012	0.081	1.20157
0.015	0.039	1.20957
0.015	0.069	1.20395
0.010	0.101	1.19760
0.011	0.115	1.19570
0.007	0.136	1.19105
0.000	0.168	1.18588

The measured compositions of the equilibrium liquid phases of the three studied systems at $T = 298.15$ K and atmospheric pressure are presented in Table 3. The samples from the methylcyclohexane-rich phase were assumed to be free of ILs; at least, the presence of ILs was not detected in the upper phase by ^{1}H NMR. Similar conclusions were obtained by other authors using other ILs and other techniques.[6,7,13] The triangular diagrams with the tie-lines for studied systems at $T = 298.15$ K are shown in Figure I, available in Supporting Information. Note that two tie-lines with similar initial compositions were carried out for each LLE, showing the repeatability of the experiments. Comparing the results of the three ternary systems, it can be seen that benzene, toluene, and ethylbenzene display partial solubility in [EMpy][ESO$_4$], and methylcyclohexane is almost immiscible with IL. Methylcyclohexane and aromatic compounds are completely soluble in all proportions. In all diagrams, the size of the immiscible zone, and therefore the tie-lines length, is large, indicating that a good separation of the aromatic compound from methylcyclohexane using [EMpy][ESO$_4$] IL could be possible.[9] On other hand, the solubility of ILs in methylcyclohexane + aromatic compound mixtures is zero or very low which makes the recycling of ILs much easier.[15] The solubility of aromatic compounds in [EMpy][ESO$_4$] decreases in the order of benzene > toluene > ethylbenzene.

Together with the LLE experimental data, Table 3 includes the corresponding values for the percent removal of aromatic

Table 3. Experimental LLE Data in Mole Fraction for the Ternary Systems Methylcyclohexane (1) + Aromatic Compound (2) + [EMpy][ESO$_4$] (3) at $T = 298.15$ K and the Percent Removal of the Aromatic Compound, Distribution Coefficient, β, and Selectivity, S, Values

alkane-rich phase		IL-rich phase		% removal of aromatic compound	β	S
x_1^I	x_2^I	x_1^{II}	x_2^{II}			
Methylcyclohexane (1) + Benzene (2) + [EMpy][ESO$_4$] (3)						
0.955	0.045	0.013	0.046	0.202	1.02	75.09
0.900	0.100	0.013	0.091	0.231	0.91	63.00
0.843	0.157	0.012	0.128	0.216	0.82	57.27
0.791	0.209	0.012	0.163	0.215	0.78	51.41
0.681	0.319	0.010	0.228	0.213	0.71	48.67
0.681	0.319	0.010	0.228	0.212	0.71	48.67
0.559	0.441	0.009	0.292	0.221	0.66	41.13
0.305	0.695	0.006	0.418	0.238	0.60	30.57
0.171	0.829	0.004	0.489	0.269	0.59	25.22
Methylcyclohexane (1) + Toluene (2) + [EMpy][ESO$_4$] (3)						
0.942	0.058	0.013	0.03	0.169	0.52	37.48
0.883	0.117	0.011	0.055	0.145	0.47	37.74
0.821	0.179	0.010	0.079	0.143	0.44	36.23
0.762	0.238	0.009	0.100	0.132	0.42	35.57
0.633	0.367	0.007	0.143	0.127	0.39	35.24
0.637	0.363	0.007	0.142	0.126	0.39	35.60
0.514	0.486	0.005	0.18	0.124	0.37	38.07
0.384	0.616	0.003	0.222	0.129	0.36	46.13
0.249	0.751	0.002	0.264	0.131	0.35	43.77
0.126	0.874	0.001	0.303	0.132	0.35	43.68
Methylcyclohexane (1) + Ethylbenzene (2) + [EMpy][ESO$_4$] (3)						
0.934	0.066	0.016	0.022	0.115	0.33	19.46
0.860	0.140	0.016	0.034	0.80	0.24	13.05
0.810	0.190	0.016	0.042	0.73	0.22	11.19
0.742	0.258	0.015	0.055	0.73	0.21	10.55
0.610	0.390	0.013	0.08	0.71	0.21	9.63
0.616	0.384	0.014	0.078	0.70	0.20	8.94
0.491	0.509	0.011	0.101	0.68	0.20	8.86
0.354	0.646	0.008	0.126	0.65	0.20	8.63
0.221	0.779	0.004	0.153	0.71	0.20	10.85

compound expressed as 100 times the amount of aromatic compound extracted in the IL-rich phase divided by the initial total amount of aromatic compound, the distribution coefficient, β, and the selectivity, S defined below:

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

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

where x_1^I and x_2^I are the mole fractions of methylcyclohexane and aromatic compound, respectively, in the upper phase (methylcyclohexane-rich phase), and x_1^{II} and x_2^{II} are the mole fractions of methylcyclohexane and aromatic compound, respectively, in the lower phase (IL-rich phase). The variations of S and β with the composition of the aromatic compounds in the raffinate phase are plotted in Figure 1. The distribution coefficients of the aromatic compounds decrease with increasing composition of the aromatic compound in the methylcyclohexane-rich phase for all studied systems. Comparing the results of the three ternary systems, it can be seen that selectivity and distribution coefficient values decrease in the order of benzene > toluene > ethylbenzene, in the same way of the miscible region. This behavior indicates that the larger one is the alkyl chain of the aromatic compound and the smaller ones are both parameters. All values of the selectivity for the studied systems are higher than unity and better than the ones obtained with other solvents (e.g., N-formylmorpholine),[28,29] which confirms that the aromatic compound extraction is possible with [EMpy][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. This is the reason why the percent removal of aromatic compound was included in our study, with the other parameter being less dependent on the mole fraction. In this case, similar results were obtained with both parameters. Taking into account the values of S, β, and the percent removal of aromatic compound, we can conclude that the IL [EMpy][ESO$_4$] could be used to separate benzene, toluene, and ethylbenzene from methylcyclohexane, while the more favorable results are obtained for the system containing benzene.

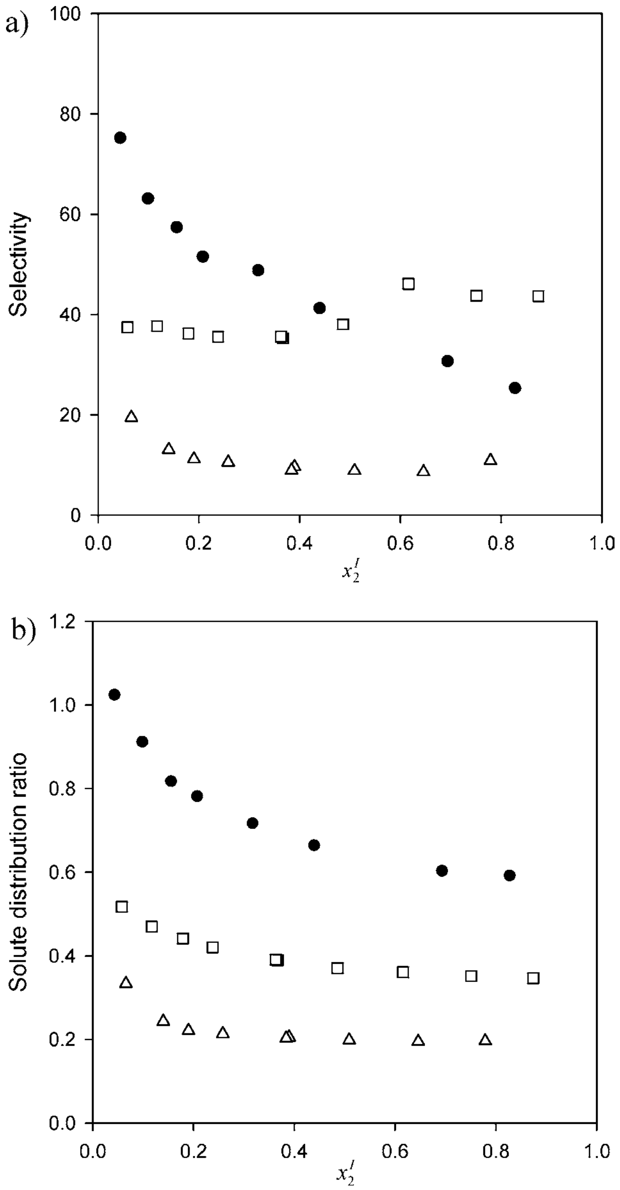

Figure 1. (a) Selectivity and (b) distribution coefficient for the ternary systems methylcyclohexane (1) + aromatic compound (2) + [EMpy][ESO$_4$], at $T = 298.15$ K, as a function of the mole fraction of the aromatic compound in the cycloalkane-rich phase. Aromatic compounds: ●, benzene; □, toluene; △, ethylbenzene.

The equations provided by Othmer−Tobias[19] and Hand[20] were used to ascertain the reliability of the experimental tie-line compositions:

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

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

where w_1^{I} and w_2^{I} are the mass fraction of methylcyclohexane and aromatic compound, respectively, in the methylcyclohexane-rich phase; w_2^{II} and w_3^{II} are the mass fraction of aromatic compound and IL, respectively, in the IL-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 plot for the studied systems is shown in Figure 2, and the parameters obtained from the proposed equations are available in the Supporting Information. It is important to mention that the higher deviations from linearity are obtained for the experimental tie-lines that present higher concentrations of the aromatic compound, when the tie-line end is closer to the binary system. The Othmer−Tobias equation gives better results than the Hand equation.

Thermodynamic Correlation. The thermodynamic model, the NRTL equation,[21] was employed to correlate the experimental LLE data. This model was not originally created for systems that involve electrolytes, but nevertheless several authors have used this model to describe their measurements of LLE with ILs.[30]

In this model, the activity coefficients are calculated as follows:

$$\ln\gamma_{\mathrm{i}} = \left(\frac{\sum_{j=1}^{n}\tau_{ji}x_jG_{ji}}{\sum_{k=1}^{n}x_kG_{ki}}\right) + \sum_{j=1}^{n}\left(\frac{x_jG_{ij}}{x_kG_{kj}}\right)\left(\tau_{ij} - \frac{\sum_{m=1}^{n}\tau_{mi}x_mG_{mi}}{\sum_{k=1}^{n}x_kG_{kj}}\right) \qquad (5)$$

where

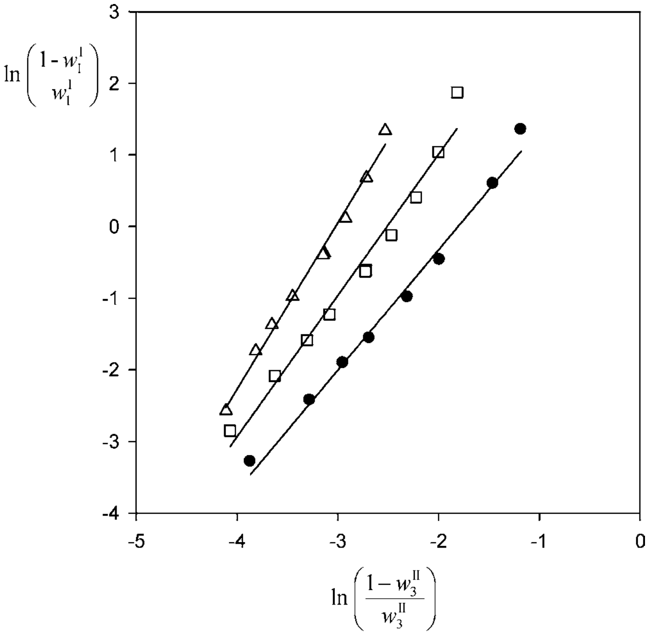

Figure 2. Othmer−Tobias plot for the systems methylcyclohexane (1) + aromatic compound (2) + [EMpy][ESO$_4$] at T = 298.15 K. Aromatic compounds: ●, benzene; □, toluene; △, ethylbenzene.

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

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

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 an adjustable parameter, in this case it will be considered fixed. For each system, several values for α_{ij} were tested (from α_{ij} = 0 to 0.5), and the best results were achieved for the values presented in Table 4. The typical values for α_{ij} are found in the range 0.2 to 0.47, but in this work the best results were achieved using values outside of this range. Some studies were found in literature where α_{ij} values outside of the typical range provide the lower deviations in the correlation of LLE of systems containing ILs.[4,5,14,15] The binary interaction parameters, Δg_{ij}, are estimated from experimental data. The objective function used minimizes the differences between the experimental and the 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 were included in the correlation.

The NRTL binary interaction parameters of the ternary systems correlated are listed in Table 4, as well as the values of the root-mean-square deviation of the composition, σx, and the mean error of the distribution coefficient, $\Delta\beta$. These deviations were calculated as follows:

$$\sigma x = 100\sqrt{\frac{\sum_{i}^{M}\sum_{j}^{N-1}(x_{ij}^{\mathrm{I,exp}} - x_{ij}^{\mathrm{I,calc}})^2 + (x_{ij}^{\mathrm{II,exp}} - x_{ij}^{\mathrm{II,calc}})^2}{2MN}} \qquad (6)$$

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

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

The experimental LLE data are plotted in Figure I (Supporting Information) together with the correlation obtained with the NRTL model. The miscible region decreases as the alkyl chain of the aromatic compound increases in the form benzene > toluene > ethylbenzene. The presence of radicals in the aromatic compound has a negative influence on the extraction, since S, β, and the percent removal of the aromatic compound decrease, which implies more stages and more quantity of ILs. The NRTL

Table 4. NRTL Binary Interaction Parameters and Deviations for LLE Data of Ternary Systems at T = 298.15 K

$i-j$	Δg_{ij} kJ·mol^{-1}	Δg_{ji} kJ·mol^{-1}	α_{ij}	σx	$\Delta\beta$
Methylcyclohexane (1) + Benzene (2) + [EMpy][ESO$_4$] (3)					
1−2	−4.1810	4.4748	0.07	0.087	1.184
1−3	225.58	10.592			
2−3	27.474	−13.141			
Methylcyclohexane (1) + Toluene (2) + [EMpy][ESO$_4$] (3)					
1−2	13.056	−11.601	0.03	0.102	1.611
1−3	171.91	−11.293			
2−3	49.578	−26.118			
Methylcyclohexane (1) + Ethylbenzene (2) + [EMpy][ESO$_4$] (3)					
1−2	18.475	−11.864	0.08	0.084	2.826
1−3	28.621	−0.9543			
2−3	57.068	−6.0648			

model fits the experimental data satisfactorily, as shown in Figure I (in Supporting Information) and Table 4, presenting small deviations. It is important to comment that the NRTL model calculates little quantities of IL in the upper phase for the ternary systems containing benzene and toluene at high aromatic compound compositions and that it is more difficult to correlate systems with less miscible regions.

Conclusions

In this work, LLE for the ternary systems methylcyclohexane (1) + benzene (2) + [EMpy][ESO_4] (3), methylcyclohexane (1) + toluene (2) + [EMpy][ESO_4] (3), and methylcyclohexane (1) + ethylbenzene (2) + [EMpy][ESO_4] (3) were determined at T = 298.15 K and atmospheric pressure. From the experimental data, the selectivity, percent removal of aromatic compound, and solute distribution ratio were calculated. The miscible region of the studied ternary systems decreases in the form benzene > toluene > ethylbenzene, and this trend is also followed by the calculated parameters S, percent removal of the aromatic compound, and β. The values of the selectivity for the studied systems are higher than unity and better than the ones obtained with other solvents, which confirms that the aromatic compound extraction for these systems is possible with [EMpy][ESO_4]. On the other hand, the values of the distribution coefficients are less than one, and this means that high amounts of ILs would be necessary for the separation of the studied mixtures.

The Othmer−Tobias and Hand equations were used to ascertain the reliability of the experimental data, obtaining good results, and the NRTL model was satisfactorily applied to correlate the LLE data.

Supporting Information Available:

Othmer−Tobias and Hand equation parameters and experimental and calculated LLE for the ternary systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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