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Liquid−Liquid Equilibria for the Ternary Systems {Heptane + Toluene + *N*-Butylpyridinium Tetrafluoroborate or *N*-Hexylpyridinium Tetrafluoroborate} at $T = 313.2$ K

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Liquid−liquid equilibrium (LLE) data for the ternary systems {heptane + toluene + *N*-butylpyridinium tetrafluoroborate ([bpy]BF_4)} and {heptane + toluene + *N*-hexylpyridinium tetrafluoroborate ([hpy]BF_4)} at 313.2 K and atmospheric pressure are reported. The degree of consistency of the experimental LLE data was ascertained by applying the Othmer−Tobias correlation. To check the feasibility of using the [bpy]BF_4 and [hpy]BF_4 ionic liquids as solvents in aromatic separation processes, their values of the distribution ratio and separation factor over the whole range of compositions were plotted and compared with those of sulfolane. In addition, the LLE data were successfully correlated with the thermodynamic NRTL model.

Introduction

Ionic liquids (ILs) have been proposed as environmentally friendly replacements for conventional organic solvents in the recovery of aromatics (e.g., benzene, toluene, and xylenes) from refinery process streams.[1,2] Because of the important industrial application of aromatic separation processes, many investigators have studied the liquid−liquid equilibria (LLEs) for ternary systems containing ILs, aromatics, and aliphatic hydrocarbons.[3−18] Almost all of the literature LLE data concern ternary systems containing ILs that have shown considerably lower values of selectivity and/or extractive capacity than those of sulfolane, which is the most popular solvent in aromatic separation processes. However, it is a combination of both high selectivity and high extractive capacity that make a solvent appropriate for use. The 4-methyl-*N*-butylpyridinium tetrafluoroborate ([bmpy-]BF_4) IL is among the few ILs that have shown both higher selectivity and higher extractive capacity than sulfolane.[7] To our knowledge, only one other article, by Abu-Eishah and Dowaidar,[12] deals with ternary LLE data that include as the extraction solvent a pyridinium-based tetrafluoroborate. Thus, experimental LLE data for {aliphatic hydrocarbon + aromatic hydrocarbon + pyridinium-based tetrafluoroborate} ternary systems is very scarce. Because of this, and as a continuation of our previous investigation,[19−21] the objective of this work was the measurement of LLE data for the ternary systems {heptane + toluene + *N*-butylpyridinium tetrafluoroborate ([bpy]BF_4)} and {heptane + toluene + *N*-hexylpyridinium tetrafluoroborate ([hpy]BF_4)} at 313.2 K and atmospheric pressure. This temperature was set for the experiments to allow a comparison of our results with those previously reported in the literature for the ternary system {heptane + toluene + [bmpy]BF_4)}.[7] The extractive capacity and selectivity for the studied ILs were calculated from the LLE data. The reliability of the experimentally measured LLE data was tested using the Othmer−Tobias correlation. Finally, the LLE data were correlated by the nonrandom two-liquid (NRTL) model.

Experimental Section

Heptane and toluene over molecular sieves, with water mass fractions less than 0.00005, were supplied by Sigma-Aldrich with mass fraction purity greater than 0.995 and 0.997, respectively. The ILs ([bpy]BF_4 and [hpy]BF_4) were supplied by Iolitec GmbH with quoted mass fraction purities greater than 0.99, bromide mass fractions less than 0.0001, and water mass fractions less than 0.0001. All chemicals were used as received without further purification. To prevent hydration, they were kept in their original tightly closed bottles in a desiccator before use. When any chemicals were used, they were always manipulated inside a glovebox under a dry nitrogen atmosphere.

The LLE experiments were performed in 8 mL vials with screw caps providing hermetic sealing. Mixtures of known masses of heptane/toluene feed were transferred to tared vials. After the vials were reweighed, the IL ([bpy]BF_4 or [hpy]BF_4) was gravimetrically added to the feed. The vials were then placed in a shaking incubator at 313.2 K with a shaking speed of 800 rpm for 5 h to reach the thermodynamic equilibrium. Finally, to ensure complete phase separation, the vials were left to settle overnight at a constant temperature of 313.2 K in a dry bath. Every weighing involved in the experimental work was carried out on a Mettler Toledo AB104 balance with a precision of ± 0.0001 g. The uncertainties in the temperature measurements were ± 0.1 K.

Samples from the upper layers (hydrocarbon-rich phases) were analyzed using a Bruker Avance 500 MHz NMR spectrometer. The ^{1}H NMR analysis proved that the two ILs were absent in the upper layers. Thus, gas chromatographic analyses of each layer plus an overall mass balance on hydrocarbons in the mixture were done to determine the phase compositions. Approximately 50 μL samples from the lower and upper layers were carefully taken with disposable Pasteur micropipets, dissolved in 1 mL of acetone, and analyzed using a gas chromatograph (Varian model GC 430) equipped with a flame ionization detector (FID), a 30 m × 0.250 mm (film thickness = 0.25 μm) CP-Sil 8CB wall-coated open tubular column (Chrompack), a 5 m × 0.250 mm uncoated fused silica precolumn to collect the ILs present in the lower layers, an

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Table 1. Experimental LLE Data on Mole Fractions (x), Solute Distribution Ratios (D_2), and Separation Factors ($\alpha_{2,1}$)

feed (global composition)		heptane-rich phase (upper layer)		IL-rich phase (lower layer)			
x_1	x_2	x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}	D_2	$\alpha_{2,1}$
Heptane (1) + Toluene (2) + $[bpy]BF_4$ (3)							
0.4712	0.0554	0.9228	0.0772	0.0053	0.0330	0.427	74.4
0.4193	0.1642	0.7674	0.2326	0.0050	0.0828	0.356	54.6
0.3717	0.2621	0.6322	0.3678	0.0039	0.1126	0.306	49.6
0.3045	0.3902	0.4850	0.5150	0.0052	0.1833	0.356	33.2
0.2455	0.5100	0.3621	0.6379	0.0047	0.2461	0.386	29.7
0.1952	0.6102	0.2679	0.7321	0.0039	0.2894	0.395	27.2
0.1581	0.6861	0.2032	0.7968	0.0030	0.3054	0.383	26.0
0.1217	0.7583	0.1470	0.8530	0.0023	0.3119	0.366	23.4
Heptane (1) + Toluene (2) + $[hpy]BF_4$ (3)							
0.4687	0.0551	0.9337	0.0663	0.0244	0.0444	0.670	25.6
0.4140	0.1740	0.7826	0.2174	0.0229	0.1279	0.588	20.1
0.3699	0.2611	0.6668	0.3332	0.0222	0.1767	0.530	15.9
0.3042	0.3923	0.5153	0.4847	0.0233	0.2695	0.556	12.3
0.2425	0.5161	0.3746	0.6254	0.0208	0.3328	0.532	9.6
0.1981	0.6045	0.2892	0.7108	0.0185	0.3949	0.556	8.7
0.1515	0.6974	0.2057	0.7943	0.0143	0.4522	0.569	8.2
0.1256	0.7491	0.1652	0.8348	0.0136	0.5064	0.607	7.4

isothermal split/splitless injector (Varian model 1177), and an autosampler (Varian model CP-8400). Varian Galaxie chromatography software was used to obtain the chromatographic areas for the hydrocarbon components. The oven temperature was fixed at 323 K. The injector port and detector temperatures were held at 523 K. The flow rate of the carrier gas (helium) was kept at 1 mL·min^{-1}.

An area normalization method with response factors was carried out to determine the hydrocarbon concentration ratio in each layer. The gas chromatography response factors for the hydrocarbons were calculated by using standard mixture samples of pure heptane and toluene. The composition of these standard samples were obtained through weighing with an electronic balance having a precision of ± 0.0001 g. Toluene in the mixture was set as the standard, and its response factor was set to 1.0. The response factor for heptane was then calculated using the renormalization method before every run of samples to ensure measurement accuracy. The coefficient of variation of the measured response factors was less than 0.5 %, so the estimated uncertainties in the determination of the hydrocarbon molar compositions in the upper and lower layers should be less than 0.001. All of the samples were injected six times, and the average compositions are reported in our results.

Results and Discussion

The experimental LLE data for the ternary systems {heptane + toluene + $[bpy]BF_4$} and {heptane + toluene + $[hpy]BF_4$} at $T = 313.2$ K and atmospheric pressure are given in Table 1 and plotted on triangular diagrams in Figures 1 and 2, respectively. As can be seen, the tie lines slope upward from right to left, reflecting the much higher solubility of toluene in heptane (upper layer) than in either of the ILs (lower layer). However, both ternary systems show a high ratio of desired product (toluene) to diluent (heptane) in the extract phase (lower layer). The solubility of heptane in each of the IL-rich phases is relatively low, with the lower solubility of heptane in the IL-rich phase showed by the ternary system {heptane + toluene + $[bpy]BF_4$}. On the other hand, both solvents (ILs) have a negligible solubility in either of the other two components (upper layer).

The feasibility of using the $[bpy]BF_4$ and $[hpy]BF_4$ ILs as solvents to perform extraction of toluene from mixtures with heptane was evaluated using the toluene distribution ratio (D_2) and the separation factor ($\alpha_{2,1}$), which were calculated from the experimental LLE data as follows:

$$D_2 = \frac{x_2^{II}}{x_2^{I}} \tag{1}$$

$$\alpha_{2,1} = \frac{x_2^{II}x_1^{I}}{x_2^{I}x_1^{II}} \tag{2}$$

where x is the mole fraction, superscripts I and II refer to the heptane-rich and IL-rich phases, respectively, and subscripts 1 and 2 denote heptane and toluene, respectively. The values of D_2 and $\alpha_{2,1}$ are shown in Table 1 together with the experimental LLE data.

The distribution ratios and separation factors for the two ternary systems as functions of the toluene mole fraction in the heptane-rich phase are shown in Figures 3 and 4, respectively. Comparisons with literature data for the ternary systems {heptane + toluene + $[bmpy]BF_4$} and {heptane + toluene + sulfolane} are also made.[7] As can be seen from Figure 3, the

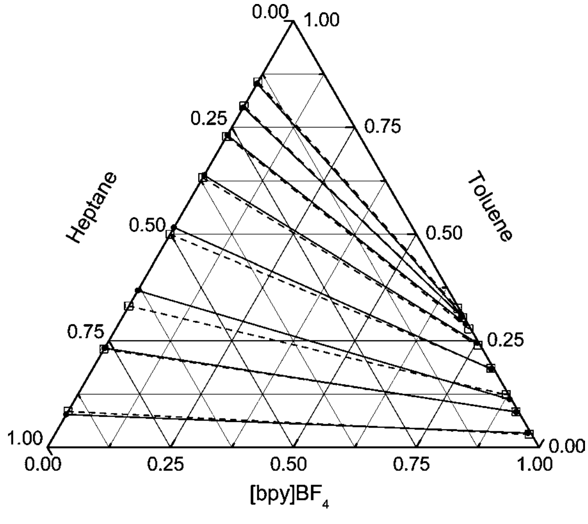

Figure 1. Experimental and calculated LLE data for the ternary system heptane (1) + toluene (2) + $[bpy]BF_4$ (3) at $T = 313.2$ K with an rmsd of 0.0096. Solid lines and solid circles represent experimental tie lines, and dashed lines and open squares represent data calculated using the NRTL model.

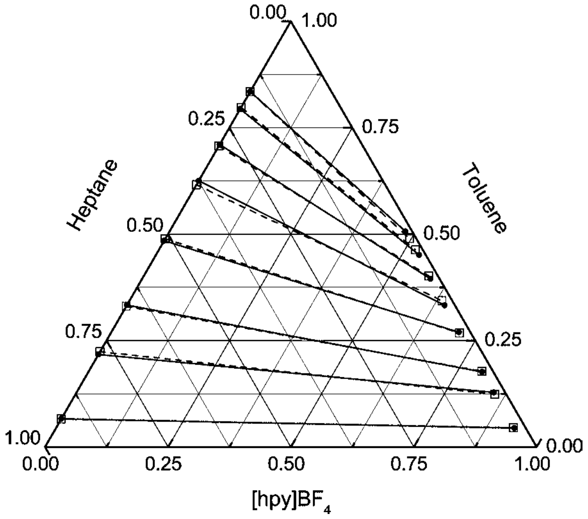

Figure 2. Experimental and calculated LLE data for the ternary system heptane (1) + toluene (2) + [hpy]BF_4 (3) at $T = 313.2$ K with an rmsd of 0.0056. Solid lines and solid circles represent experimental tie lines, and dashed lines and open squares represent data calculated using the NRTL model.

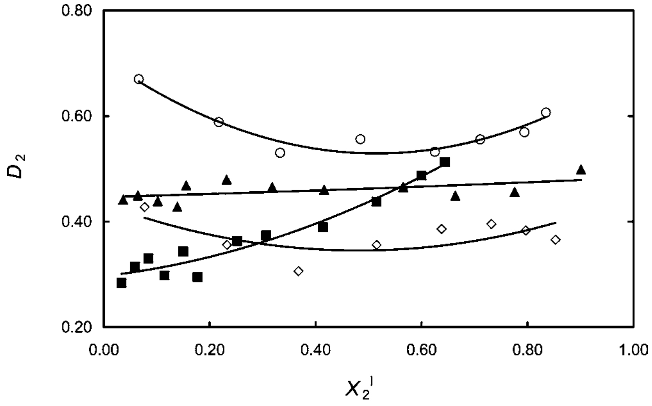

Figure 3. Distribution ratio of toluene for the ternary systems at $T = 313.2$ K: ◇, heptane (1) + toluene (2) + [bpy]BF_4 (3); ○, heptane (1) + toluene (2) + [hpy]BF_4 (3); ▲, heptane (1) + toluene (2) + [bmpy]BF_4 (3) (from ref 7); ■, heptane (1) + toluene (2) + sulfolane (3) (from ref 7).

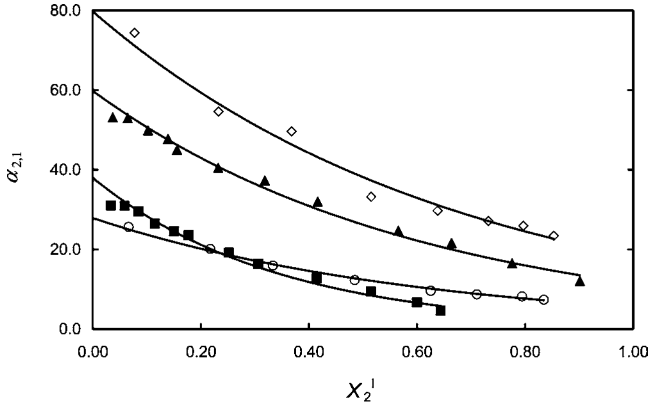

Figure 4. Separation factor for the ternary systems at $T = 313.2$ K: ◇, heptane (1) + toluene (2) + [bpy]BF_4 (3); ○, heptane (1) + toluene (2) + [hpy]BF_4 (3); ▲, heptane (1) + toluene (2) + [bmpy]BF_4 (3) (from ref 7); ■, heptane (1) + toluene (2) + sulfolane (3) (from ref 7).

values of the distribution ratio for the three ILs grow in the order [bpy]BF_4 < [bmpy]BF_4 < [hpy]BF_4, but only the [hpy]BF_4 IL shows larger values of D_2 than sulfolane over the whole range of composition. On the other hand, the values of the separation factor for the three ILs (Figure 4) grow in the order [hpy]BF_4 < [bmpy]BF_4 < [bpy]BF_4. As can also be seen from Figure 4, the [bpy]BF_4 and [bmpy]BF_4 ILs show larger separation factor values than sulfolane over the whole range of composition, but the [hpy]BF_4 IL shows slightly larger values of the separation factor only for toluene mole fractions in the heptane-rich phase greater (x_2^{I}) than 0.20. Therefore, none of the three ILs presents both a higher distribution ratio and a higher separation factor than those of sulfolane over the whole range of compositions. However, the [bpy]BF_4 and [bmpy]BF_4 ILs could be considered as alternative solvents for extraction of aromatics from aliphatic hydrocarbons in the low composition range (i.e., $x_2^{\mathrm{I}} < 0.20$), since their distribution ratios and separation factors are clearly higher than those of sulfolane at these compositions.

Table 2. Constants of the Othmer−Tobias Correlation (*a*, *b*), Regression Coefficients (R^2), and Standard Deviations (σ)

a	*b*	R^2	σ
Heptane (1) + Toluene (2) + [bpy]BF_4 (3)			
−2.4460	0.6127	0.9765	0.1461
Heptane (1) + Toluene (2) + [hpy]BF_4 (3)			
−1.8717	0.6210	0.9980	0.0427

Table 3. Values of the NRTL Parameters Obtained from the LLE Data by Regression

components	NRTL parameters		
$i-j$	$[(g_{ij} - g_{ii})/R]$/K	$[(g_{ji} - g_{jj})/R]$/K	α_{ij}
Heptane (1) + Toluene (2) + [bpy]BF_4 (3)			
1−2	131.99	−177.24	0.3033
1−3	−9.5921	545.15	0.1429
2−3	2539.6	−593.53	0.1381
Heptane (1) + Toluene (2) + [hpy]BF_4 (3)			
1−2	92.818	0.6449	0.3004
1−3	259.73	3692.7	0.3012
2−3	1577.5	−436.28	0.1887

The reliability of the experimentally measured LLE data can be ascertained by applying the Othmer−Tobias correlation:[22]

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

where w_3^{II} is the mass fraction of IL (3) in the IL-rich phase (lower layer), w_1^{I} is the mass fraction of heptane (1) in the heptane-rich phase (upper layer), and *a* and *b* are the fitting parameters of the Othmer−Tobias correlation. The linearity of the plot indicates the degree of consistency of the data. The parameters of the Othmer−Tobias correlation are given in Table 2. The regression coefficients (R^2) very close to unity and the small values of the standard deviation (σ) presented in Table 2 indicate the high degree of consistency of the experimental LLE data.

The NRTL model[23] was used to correlate the LLE data in the present work, as it has proven to have adequate correlating capability with respect to ternary and binary LLE data for systems that contain ILs.[24] In this model, the two binary interaction parameters $(g_{ij} - g_{ii})/R$ and $(g_{ji} - g_{jj})/R$ were calculated using an ASPEN Plus Simulator. The regression method used in the ASPEN simulator was the generalized least-squares method based on maximum likelihood principles. The Britt−Luecke algorithm[25] was employed to obtain the model parameters with the Deming initialization method. The regression convergence tolerance was set to 0.0001. The value of the third nonrandomness parameter, α_{ij}, in the NRTL model was subject to optimization between 0 and 1.

Table 3 shows the values of the fitting parameters obtained using the NRTL model to correlate the experimental LLE data for the ternary systems {heptane + toluene + [bpy]BF_4} and {heptane + toluene + [hpy]BF_4}. The calculated tie lines from the correlation based on the NRTL model are plotted in Figures 1 and 2 together with the experimental tie-line data. The values of the root-mean-square deviation (rmsd) for the two ternary systems are listed in the captions of Figures 1 and 2. The rmsd is defined as

$$\text{rmsd} = \left\{ \frac{\sum_i \sum_l \sum_m (x_{ilm}^{\text{exptl}} - x_{ilm}^{\text{calcd}})^2}{6k} \right\}^{1/2} \qquad (4)$$

where x is the mole fraction and the subscripts i, l, and m represent the component, phase, and tie line, respectively. The value of k designates the number of tie lines.

Conclusions

In this work, liquid−liquid equilibria data for the ternary systems {heptane + toluene + [bpy]BF_4} and {heptane + toluene + [hpy]BF_4} were determined experimentally at 313.2 K and atmospheric pressure. The corresponding values of the distribution ratio and separation factor were calculated and compared with those reported in the literature for the ternary systems {heptane + toluene + [bmpy]BF_4} and {hexane + benzene + sulfolane}. The degree of consistency of the experimental LLE data was ascertained by applying the Othmer−Tobias correlation.

The values of distribution ratio and separation factor for the ternary systems using the [bpy]BF_4, [hpy]BF_4, and [bmpy]BF_4 ILs are not simultaneously higher than those for the ternary system involving sulfolane over the whole range of compositions. However, the values of the distribution ratio and separation factor for the systems containing the [bpy]BF_4 and [bmpy]BF_4 ILs are clearly higher than those for the ternary system containing sulfolane in the low range of toluene composition. In addition, the ILs are totally immiscible in the hydrocarbon-rich phase, which would make their recovery and reuse easier and cheaper than when the aromatic separation process is carried out using sulfolane. In summary, the [bpy]BF_4 and [bmpy]BF_4 ILs could be considered as alternative solvents for extraction of aromatics from aliphatic/aromatic mixtures when the aromatic concentration in the feed is low.

The NRTL model was used to satisfactorily correlate the experimental LLE data for the two studied ternary systems.

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