Liquid−Liquid Equilibria for Systems Composed by 1-Methyl-3-octylimidazolium Tetrafluoroborate Ionic Liquid, Thiophene, and *n*-Hexane or Cyclohexane

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Liquid−liquid equilibrium data have been determined experimentally for {1-methyl-3-octylimidazolium tetrafluoroborate + thiophene + hexane} and {1-methyl-3-octylimidazolium tetrafluoroborate + thiophene + cyclohexane} ternary systems at 298.15 K. The compositions of the ends of the tie-lines were obtained by gas chromatographic analysis of phases at equilibrium. Data have been adequately correlated using the nonrandom two-liquid (NRTL) activity coefficient model despite this being an equation intended for nonelectrolyte solutions.

Introduction

During the last few years, ionic liquids (ILs) have received attention in academia and industry worldwide as potential alternatives to conventional organic solvents in a variety of industrial processes.[1,2] ILs are salts that consist of bulky organic cations and organic or inorganic anions. These ionic solvents are composed entirely of ions and strongly resemble ionic melts that may be produced by heating metallic salts but are liquid at temperatures as low as 177 K. They are also colorless, have low viscosities, and are easily handled.[3] The practical differences with molten salts were sufficient to justify a separately identified niche for ionic liquids. These liquids exhibit a wide liquid range and thermal stability, are immiscible with a number of organic solvents and/or water, and are good solvents for a wide range of inorganic, organic, and polymeric materials. Moreover, they have negligible vapor pressure. Such a low volatility may be the single most attractive property of ILs to be used as solvents.

Liquid−liquid extraction has often been a favored choice of process engineers for the development of separation processes. One of the primary driving forces behind research into ILs is the perceived benefit of substituting conventional industrial solvents, most of which are volatile organic compounds (VOCs), with nonvolatile ionic liquids. Replacement of traditional extraction solvents by ionic liquids would prevent the emission of VOCs, a major source of environmental pollution.

Typical compounds of gasoline are hydrocarbons as hexane, cyclohexane, and thiophene derivatives. With the aim of focusing our research on desulfurization of oil, in this work liquid−liquid equilibria (LLE) of {1-methyl-3-octylimidazolium tetrafluoroborate + thiophene + *n*-hexane} and {1-methyl-3-octylimidazolium tetrafluoroborate + thiophene + cyclohexane} ternary systems are determined at 298.15 K. The experimental data are correlated with the nonrandom two-liquid (NRTL)[4] activity coefficient model.

Experimental Section

Chemicals. Hexane (Fluka, mass fraction > 99.0 %), cyclohexane (Riedel-de Haën, purum, mass fraction > 99.5 %), and thiophene (Aldrich, purum, mass fraction > 99.5 %) were used as received from the supplier without further purification. The ionic liquid 1-methyl-3-octylimidazolium tetrafluoroborate, [C_8mim][BF_4], was synthesized in our laboratory as explained below. The purities of hexane, cyclohexane, and thiophene were verified by gas chromatography. The purity of the IL was verified by ^{1}H NMR spectroscopy. Further information about the pure components, experimental densities, refractive indices, and water contents, along with values published by other authors,[5−8] are shown in Table 1.

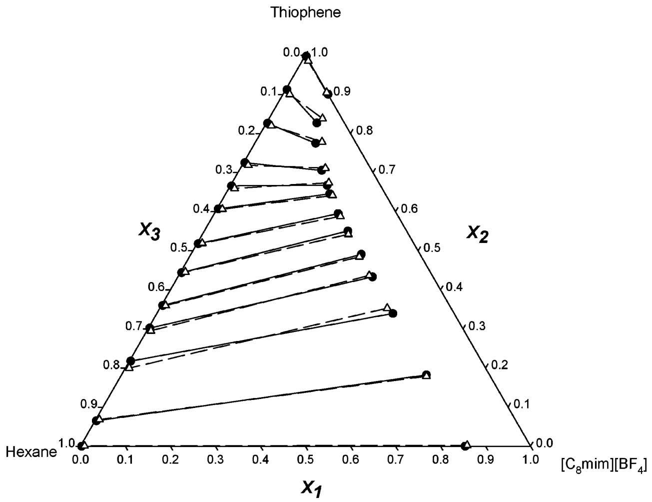

Figure 1. Experimental tie-lines (●, solid line) for the LLE of the ternary system {[C_8mim][BF_4] (1) + thiophene (2) + *n*-hexane (3)} at 298.15 K. The corresponding tie-lines correlated by means of the NRTL equation, with $\alpha = 0.3$, are also plotted (△, long dash).

Preparation of [C_8min][BF_4]. 1-Methylimidazole was reacted with an excess of 1-bromooctane to produce 1-methyl-3-octylimidazolium bromide. The [C_8mim][Br] was reacted with sodium tetrafluoroborate in aqueous solution to produce [C_8min][BF_4]. The later is immiscible with water, and thus two phases appeared. The ionic liquid phase was decanted and dissolved in dichloromethane, and this mixture was washed several times with water. A rotary evaporator was used first to remove the dichloromethane and water, and then purification was completed under a vacuum. Details of preparation have been published before.[9]

Procedure. All weighing was carried out in a Mettler Toledo AT 261 balance with an accuracy of ± 10^{-4} g. Water content was measured using a Karl−Fischer titration method in a

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Table 1. Water Content, Density (ρ), and Refractive Index (n_D) of the Pure Components at 298.15 K and Atmospheric Pressure

		water	ρ (g·cm^{-3})		n_D	
component	CAS no.	ppm	exptl	lit.	exptl	lit.
cyclohexane	110-82-7	45	0.77376	0.77389[5]	1.42403	1.42354[5]
hexane	110-54-3	75	0.65506	0.65484[5]	1.37287	1.37226[5]
thiophene	110-02-1	338	1.05850	1.05887[6]	1.52581	1.52572[6]
[C$_8$mim][BF$_4$]	244193-52-0	51	1.10442	1.103506[7]	1.43329	1.4322[8]

Metrohm 737 KF coulometer. Densities were measured in an Anton Paar DMA 60/602 densimeter. The uncertainty in the measurement is ± 10^{-5} g·cm^{-3}. Refractive indices were measured in an ATAGO RX-5000 refractometer. The uncertainty in the measurement is ± $4 \cdot 10^{-5}$.

For the determination of the experimental tie-lines, mixtures with compositions inside the immiscible region of the systems were introduced into 30 mL glass jacketed vessels, with magnetic stirrers, and closed. The jackets were connected to a thermostat bath (Julabo F12) to maintain a constant temperature of 298.15 K in the vessels. Repeated experiments showed that equilibrium was established after about 2 h of stirring (to ensure good contact between both phases) and a minimum of 4 h to settle. Samples of both layers were then withdrawn using syringes, and thiophene and hydrocarbon compositions were analyzed by gas chromatography using an internal standard method. Ionic liquid compostion was calculated by difference. The gas chromatograph used was an HP 6890 series equipped with a thermal conductivity detector (TCD), an HP5 capillary column (30 m × 0.32 mm × 0.25 μm), and an empty precolumn to protect the column and collect the ionic liquid that could not be retained by liner. Helium was used as mobile phase, and the injection volume was 1 μL with a split ratio of 1:100. The GC operating conditions are given in Table 2. The estimated uncertainty in the determination of mole fraction compositions is ± 0.004 in the hydrocarbon-rich phase and ± 0.005 in the IL-rich phase.

Results and Discussion

Experimental LLE Data. The compositions of the experimental tie-lines for {1-methyl-3-octylimidazolium tetrafluoroborate + thiophene + hexane} and {1-methyl-3-octylimidazolium tetrafluoroborate + thiophene + cyclohexane} ternary systems at 298.15 K are reported in Tables 3 and 4, respectively. Values of the solute distribution ratio (β) and selectivity (S) are also shown in those tables. These parameters are defined as follows:

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

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

Table 2. Operating Conditions for the Gas Chromatograph

column	HP-5
detector type	TCD
detector temperature	523.15 K
injector temperature	523.15 K
oven temperature	2.2 min at 333.15 K $\xrightarrow{\text{ramp } 10\ \text{K·min}^{-1}}$ 373.15 K, isothermal for 1.2 min
carrier gas	He
flow rate	1.3 mL·min^{-1}

Table 3. Compositions of Experimental Tie-Lines, Solute Distribution Ratios (β), and Selectivities (S) for {[C$_8$mim][BF$_4$] (1) + Thiophene (2) + Hexane (3)} at 298.15 K

hydrocarbon-rich phase			IL-rich phase				
x_1	x_2	x_3	x_1	x_2	x_3	β	S
0.000	0.000	1.000	0.855	0.000	0.146	–	–
0.000	0.065	0.935	0.677	0.182	0.140	2.80	18.69
0.000	0.218	0.782	0.524	0.339	0.136	1.56	8.93
0.000	0.302	0.698	0.432	0.433	0.135	1.43	7.43
0.000	0.360	0.640	0.379	0.491	0.131	1.36	6.68
0.000	0.444	0.556	0.319	0.550	0.131	1.24	5.28
0.000	0.518	0.482	0.275	0.595	0.130	1.15	4.26
0.000	0.607	0.393	0.231	0.646	0.123	1.06	3.39
0.000	0.666	0.334	0.215	0.667	0.118	1.00	2.83
0.000	0.725	0.275	0.183	0.706	0.111	0.97	2.41
0.000	0.826	0.174	0.135	0.775	0.090	0.94	1.81
0.000	0.912	0.088	0.112	0.827	0.061	0.91	1.30
0.000	1.000	0.000	0.100	0.900	0.000	0.90	–

Table 4. Compositions of Experimental Tie-Lines, Solute Distribution Ratios (β), and Selectivities (S) for {[C$_8$mim][BF$_4$] (1) + Thiophene (2) + Cyclohexane (3)} at 298.15 K

hydrocarbon-rich phase			IL-rich phase				
x_1	x_2	x_3	x_1	x_2	x_3	β	S
0.052	0.000	0.948	0.792	0.000	0.208	–	–
0.048	0.066	0.886	0.676	0.126	0.198	1.90	8.50
0.045	0.125	0.830	0.591	0.220	0.189	1.76	7.71
0.043	0.234	0.723	0.470	0.348	0.182	1.49	5.91
0.042	0.376	0.583	0.349	0.483	0.169	1.28	4.43
0.040	0.494	0.466	0.297	0.540	0.164	1.09	3.12
0.033	0.606	0.361	0.233	0.619	0.149	1.02	2.47
0.031	0.671	0.299	0.206	0.659	0.136	0.98	2.16
0.024	0.810	0.166	0.142	0.776	0.083	0.96	1.92
0.020	0.890	0.091	0.121	0.827	0.053	0.93	1.61
0.000	1.000	0.000	0.100	0.900	0.000	0.90	–

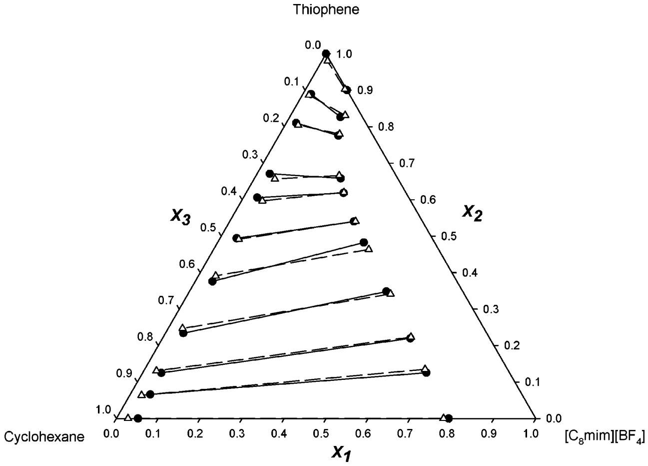

Figure 2. Experimental tie-lines (●, solid line) for the LLE of the ternary system {[C$_8$mim][BF$_4$] (1) + thiophene (2) + cyclohexane (3)} at 298.15 K. The corresponding tie-lines correlated by means of the NRTL equation, with $\alpha = 0.1$, are also plotted (△, long dash).

where x is the mole fraction; subscripts 1 and 2 refer to hydrocarbon (inert) and thiophene (solute); and superscripts I and II indicate the hydrocarbon-rich phase and the IL-rich phase, respectively. The corresponding triangular diagrams with the experimental tie-lines for each system are shown in Figures 1 and 2. Analogously, Figures 3 and 4 show the solute distribution ratios and selectivities plotted against the mole fraction of solute in the hydrocarbon-rich phase.

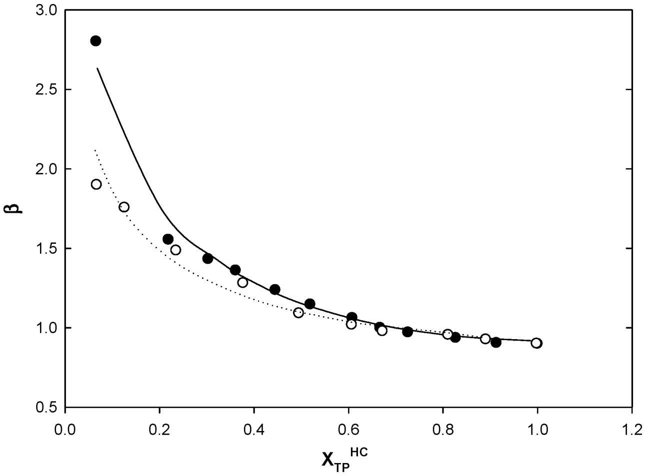

Figure 3. Solute distribution ratio as a function of the molar fraction of solute in the hydrocarbon-rich phase (X_{TP}^{HC}). ●, Experimental and ___, calculated with NRTL (α = 0.3) values for the {[C$_8$mim][BF$_4$] (1) + thiophene (2) + *n*-hexane (3)} ternary system. ○, Experimental and - - -, calculated with NRTL (α = 0.1) values for the {[C$_8$mim][BF$_4$] (1) + thiophene (2) + cyclohexane (3)} ternary system.

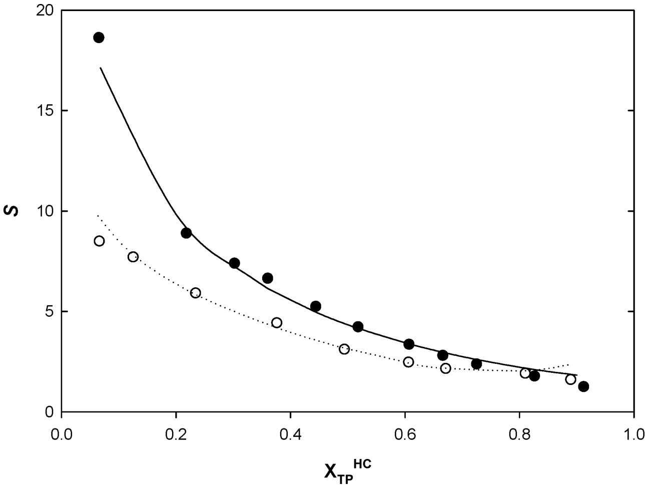

Figure 4. Selectivity as a function of the molar fraction of solute in the hydrocarbon-rich phase (X_{TP}^{HC}). ●, Experimental and ___, calculated with NRTL (α = 0.3) values for {[C$_8$mim][BF$_4$] (1) + thiophene (2) + *n*-hexane (3)}. ○, Experimental and - - -, calculated with NRTL (α = 0.1) values for the {[C8mim][BF4] (1) + thiophene (2) + cyclohexane (3)} ternary system.

Table 5. Binary Interaction Parameters (Δg_{ij}, Δg_{ji}) and Residuals (F, $\Delta\beta$) for the Correlation of {[C$_8$mim][BF$_4$] (1) + Thiophene (2) + Hexane (3)} at 298.15 K

residuals		components	parameters	
		$i-j$	Δg_{ij}/J·mol^{-1}	Δg_{ji}/J·mol^{-1}
		α = 0.1		
		1−2	−12582	25242
F	2.6709	1−3	−4735.5	18721
$\Delta\beta$	3.59	2−3	13700	−6971.3
		α = 0.2		
		1−2	−9231.6	21245
F	0.8443	1−3	1088.5	13400
$\Delta\beta$	3	2−3	−1411.1	−125.32
		α = 0.3		
		1−2	−6029.8	16296
F	0.7364	1−3	3303.9	9842.7
$\Delta\beta$	3.3	2−3	1038.1	−1209.8

Table 6. Binary Interaction Parameters (Δg_{ij}, Δg_{ji}) and Residuals (F, $\Delta\beta$) for the Correlation of {[C$_8$mim][BF$_4$] (1) + Thiophene (2) + Cyclohexane (3)} at 298.15 K

residuals		components	parameters	
		$i-j$	Δg_{ij}/J·mol^{-1})	Δg_{ji}/J·mol^{-1}
		α = 0.1		
		1−2	−19917	41836
F	1.0251	1−3	−2835.2	12480.1
$\Delta\beta$	4.4	2−3	−2318.0	−5796.1
		α = 0.2		
		1−2	−1129.6	6055.7
F	9.0007	1−3	4772.4	7597.9
$\Delta\beta$	8.60	2−3	3579.6	1204.8
		α = 0.3		
		1−2	−117.14	6893.4
F	8.3134	1−3	3579.4	6078.4
$\Delta\beta$	24	2−3	2907.8	1550.5

Correlation of LLE Data. The correlation of the experimental data was done with the NRTL[4] equation. The value of the nonrandomness parameter, α, was previously assigned to 0.1, 0.2, and 0.3. The binary interaction parameters were obtained using a computer program described by Sϕrensen,[10,11] which uses two objective functions. First, F_a, does not require any previous guess for parameters, and after convergence these parameters are used in the second function, F_b, to fit the experimental concentrations

$$F_a = \sum_k \sum_i [(a_{ik}^{I} - a_{ik}^{II})/(a_{ik}^{I} + a_{ik}^{II})]^2 + Q \sum_n P_n^{\ 2} \qquad (3)$$

$$F_b = \sum_k \min \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2 + Q \sum P_n^{\ 2} + \left[\ln\left(\frac{\hat{\gamma}_{S\infty}^{I}}{\hat{\gamma}_{S\infty}^{II}} \beta_\infty \right) \right]^2 \qquad (4)$$

where a is the activity; x is the experimental composition in mole fraction; and $\hat{x}$ is the corresponding calculated composition. Subscripts and superscripts are i for components of the mixture, j for phases (I, II), and k for tie-lines. Both functions include a penalty term (the second term) to reduce the risks of multiple solutions associated with parameters of high value, in which $Q = 10^{-6}$ for eq 3 and $Q = 10^{-10}$ for eq 4, and P_n are the adjustable parameters. F_b also includes a third term to correctly fit experimental results when working with low solute concentrations, in which $\hat{\gamma}_{S\infty}^{I}$ and $\hat{\gamma}_{S\infty}^{II}$ represent the solute activity coefficients calculated at infinite dilution in both phases and β_∞ is the solute molar distribution ratio at infinite dilution.

The quality of correlation is measured by the residual function F and the mean error of the solute distribution ratio, $\Delta\beta$

$$F = 100 \left[\sum_k \min \sum_i \sum_j \frac{(x_{ijk} - \hat{x}_{ijk})^2}{6M} \right]^{0.5} \qquad (5)$$

$$\Delta\beta = 100 \left[\sum_k \frac{((\beta_k - \hat{\beta}_k)/\beta_k)^2}{M} \right]^{0.5} \qquad (6)$$

where M refers to the number of experimental tie-lines.

Tables 5 and 6 show the binary interaction parameters and residuals corresponding to the correlation with α = 0.1, 0.2, and 0.3, for both systems studied. Correlated compositions, distribution ratios, and selectivities were included in Figures 1 to 4 for comparison with experimental values.

Conclusions

The liquid−liquid equilibrium data of the ternary systems {1-methyl-3-octylimidazolium tetrafluoroborate + thiophene +

hexane} and {1-methyl-3-octylimidazolium tetrafluoroborate + thiophene + cyclohexane} have been determined experimentally at 298.15 K.

It can be concluded from solute distribution ratios and selectivities that, from a thermodynamic point of view, the separation of thiophene from hydrocarbons as hexane or cyclohexane is feasible using [C_8min][BF_4] as solvent.

The NRTL model satisfactorily correlates the LLE experimental data of the studied systems. The α-values which led to the lowest residual values were $\alpha = 0.3$ for the system with hexane and $\alpha = 0.1$ for the system with cyclohexane. In both cases, experimental and correlated tie-lines are in very good agreement despite the fact that this equation is intended for nonelectrolyte solutions.

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