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Measurement and Correlation of Liquid−Liquid Equilibria of Two Imidazolium Ionic Liquids with Thiophene and Methylcyclohexane

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Equilibrium studies on the extraction of thiophene from its mixtures with methylcyclohexane using two imidazolium ionic liquids have been carried out. LLE data were obtained for mixtures of 1-methyl-3-octylimidazolium bis[trifluoromethylsulfonyl]imide or l-methyl-3-octylimidazolium tetrafluoroborate with thiophene and methylcyclohexane at atmospheric pressure and 298.15 K. Tie-line compositions were correlated using the NRTL equation, but considerable deviations from experimental data were found at high concentrations of thiophene. Distribution coefficients and selectivities were evaluated.

Introduction

Liquid−liquid extraction is a cheap but often effective way to simplify the problem of separating starting materials and side reaction products from desired products. Thiols, sulfides, and thiophenes are the major impurities present in crude oils and are also found in distillates and products from cracking, coking, and alkylation processes.[1] The key for using the extraction as a unit operation capable of eliminating these impurities is to find a suitable solvent that can dissolve the sulfur compounds and that can be recovered and recycled with minimum solvent loss. In looking for an adequate extracting agent, solubility and selectivity are the most important properties from a thermodynamic point of view. Additional selection criteria are stability, low cost, and nonhazardous environmental impact.

In recent years, ionic liquids (ILs) have been extensively evaluated as environmentally friendly or “green” alternatives to conventional organic solvents for a broad range of applications.[2] ILs show some unique characteristics that distinguish them from conventional organic solvents,[3] such as no effective vapor pressure, a broad liquid range, high polarity and charge density, hydrophobic or hydrophilic characteristics, unique solvating properties, they can be fine-tuned, etc. Solvent extraction has been found to be one of the fields in which the application of these compounds looks promising.[4]

Only through quantitative liquid−liquid equilibrium studies will it be possible to design separation processes to accomplish the removal of sulfur compounds. The objective of this work is to determine LLE data of 1-methyl-3-octylimidazolium bis[trifluoromethylsulfonyl]imide ([C$_8$mim][NTf$_2$]) + thiophene + methylcyclohexane and l-methyl-3-octylimidazolium tetrafluoroborate ([C$_8$mim][BF$_4$]) + thiophene + methylcyclohexane ternary systems at 298.15 K. Distribution coefficients and selectivities are evaluated, and the capability of the nonrandom two liquid (NRTL)[5] activity coefficient model to correlate obtained data is tested.

Experimental

Materials. Methylcyclohexane (Aldrich, mass fraction purity > 99 %) and thiophene (Aldrich, mass fraction purity > 99.5 %) were used as received from the supplier without further purification. Gas chromatography (GC) analysis did not detect any appreciable impurity peaks. The ILs 1-methyl-3-octylimidazolium bis[trifluoromethylsulfonyl]imide, [C$_8$mim][NTf$_2$], and l-methyl-3-octylimidazolium tetrafluoroborate, [C$_8$mim][BF$_4$], were synthesized in our laboratory as explained below. Figure 1 shows their structures. [C$_8$mim][NTf$_2$] has no melting point,[6] and the value of this property for [C$_8$mim][BF$_4$] is 185.15 K.[7] Further information about the pure components, experimental densities, refractive indices, and water contents along with values published by other authors[8−13] are shown in Table 1.

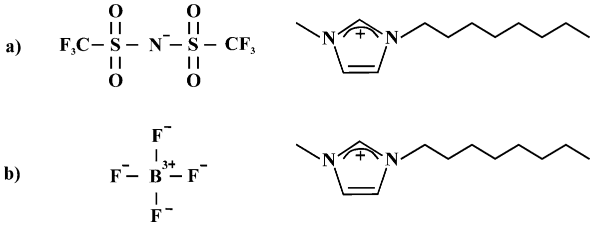

Figure 1. Structures of (a) [C$_8$mim][NTf$_2$] and (b) [C$_8$mim][BF$_4$] ionic liquids.

Production of [C$_8$min][NTf$_2$]. First, the salt [C$_8$mim][Cl] was prepared by direct alkylation of 1-methylimidazole with an excess of 1-chlorooctane, in a manner similar to that reported elsewhere.[14] This chloride ionic liquid was mixed with Li[NTf$_2$] salt in deionized water, thus obtaining the [C$_8$min][NTf$_2$] by ion metathesis which forms a dense nonaqueous phase.[15,16] Dichloromethane was added to facilitate the separation of the organic phase, with the desired ionic liquid, and the aqueous phase with the byproduct LiCl. The organic phase was washed several times with water, until there was no observance of a precipitate by adding silver(I) nitrate to the residual aqueous phase, thus indicating the absence of chloride in significant levels.[17] The dichloromethane was removed in a rotary evaporator, and the purification of the ionic liquid was completed by heating it under a high vacuum for at least 24 h (1 mbar, 80 °C). The final product was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, and its water content (Table 1) was verified by Karl Fischer titration.

Production of [C$_8$min][BF$_4$]. 1-Methylimidazole was reacted with an excess of 1-bromooctane to produce 1-methyl-3-octylimidazolium bromide. The [C$_8$mim][Br] was reacted with

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Table 1. Water Mass Fraction w_{H20}, Density ρ, and Refractive Index n_D of the Pure Components at 298.15 K and Atmospheric Pressure

			ρ/g·cm^{-3}		n_D	
component	CAS no.	$10^6 w_{H2O}$	exptl	lit.	exptl	lit.
methylcyclohexane	108-87-2	4.8	0.764970	0.76506[8]	1.42048	1.42058[8]
thiophene	110-02-1	338	1.05850	1.05887[9]	1.52581	1.52572[9]
[C_8mim][NTf_2]	178631-04-4	21	1.32076	1.31[10] 1.32[11]	1.43331	not found
[C_8mim][BF_4]	244193-52-0	51	1.10442	1.103506[12]	1.43329	1.4322[13]

Table 2. Chromatographic Conditions for Composition Analysis

column	HP-FFAP polyethylene glycol TPA (25 m × 200 μm × 0.3 μm)	
detector type	TCD	
detector temperature	523.15 K	
carrier gas	helium	
injector temperature	523.15 K	injection 1 μL
flow rate	0.5 mL·min^{-1}	split ratio: 50:1
T oven	7 min at 343.15 K, isothermal	

Table 3. Compositions of Experimental Tie-Lines, Solute Distribution Ratios β, and Selectivities *S* for {[C_8mim][NTf_2] (1) + Thiophene (2) + Methylcyclohexane (3)} at 298.15 K

IL-rich phase			hydrocarbon-rich phase				
x_1	x_2	x_3	x'_1	x'_2	x'_3	β	*S*
0.686	0.000	0.314	0.000	0.000	1.000	_	_
0.563	0.151	0.286	0.002	0.070	0.928	2.16	7.00
0.410	0.334	0.255	0.007	0.209	0.784	1.60	4.91
0.273	0.511	0.217	0.002	0.441	0.557	1.16	2.97
0.217	0.586	0.197	0.005	0.539	0.456	1.09	2.52
0.181	0.641	0.178	0.011	0.625	0.364	1.03	2.10
0.137	0.715	0.148	0.000	0.726	0.274	0.98	1.82
0.111	0.766	0.123	0.008	0.787	0.206	0.97	1.63
0.091	0.815	0.094	0.000	0.856	0.144	0.95	1.46
0.054	0.946	0.000	0.000	1.000	0.000	0.94	_

Table 4. Compositions of Experimental Tie-Lines, Solute Distribution Ratios β, and Selectivities *S* for {[C_8mim][BF_4] (1) + Thiophene (2) + Methylcyclohexane (3)} at 298.15 K

IL-rich phase			hydrocarbon-rich phase				
x_1	x_2	x_3	x'_1	x'_2	x'_3	β	*S*
0.808	0.000	0.192	0.000	0.000	1.000		
0.665	0.147	0.188	0.000	0.090	0.910	1.63	7.91
0.515	0.298	0.187	0.005	0.223	0.772	1.34	5.52
0.414	0.408	0.178	0.000	0.353	0.647	1.16	4.20
0.355	0.478	0.167	0.003	0.471	0.525	1.01	3.19
0.250	0.605	0.145	0.005	0.664	0.331	0.91	2.08
0.188	0.688	0.124	0.000	0.754	0.246	0.91	1.81
0.157	0.738	0.105	0.000	0.813	0.187	0.91	1.62
0.135	0.777	0.088	0.000	0.865	0.135	0.90	1.38
0.100	0.900	0.000	0.000	1.000	0.000	0.90	_

Table 5. Binary Interaction Parameters Δg_{ij} and Δg_{ji} and Root-Mean-Square Deviations *F*, $\Delta\beta$ for the Correlation of {[C_8mim][NTf_2] (1) + Thiophene (2) + Methylcyclohexane (3)} at 298.15 K

		components	parameters	
residuals		*i*−*j*	Δg_{ij}/J·mol^{-1}	Δg_{ji}/J·mol^{-1}
		$\alpha = 0.1$		
		1−2	−12939	25683
F	3.6547	1−3	−7916.2	25235
$\Delta\beta$	64.3	2−3	8642.9	−4527.5
		$\alpha = 0.2$		
		1−2	−6557.1	16092
F	2.5990	1−3	−1197.9	12542
$\Delta\beta$	97.50	2−3	1991.7	879.59
		$\alpha = 0.3$		
		1−2	−5464.5	14610
F	1.1332	1−3	1218.6	11023
$\Delta\beta$	91.9	2−3	554.44	456.92

Table 6. Binary Interaction Parameters Δg_{ij} and Δg_{ji} and Residuals *F* and $\Delta\beta$ for the Correlation of {[C_8mim][BF_4] (1) + Thiophene (2) + Methylcyclohexane (3)} at 298.15 K

		components	parameters	
residuals		*i*−*j*	Δg_{ij}/J·mol^{-1}	Δg_{ji}/J·mol^{-1}
		$\alpha = 0.1$		
		1−2	−15527	30681
F	1.1310	1−3	−5089.8	25483
$\Delta\beta$	34.2	2−3	−9116.0	7934.3
		$\alpha = 0.2$		
		1−2	−7946.1	18869
F	1.0150	1−3	414.17	14395
$\Delta\beta$	38.00	2−3	−3016.3	1573.0
		$\alpha = 0.3$		
		1−2	−5168.9	14482
F	0.975	1−3	2752.0	10630
$\Delta\beta$	42.3	2−3	−353.73	−532.86

sodium tetrafluoroborate in aqueous solution to produce [C_8-min][BF_4]. The latter 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 vacuum. Details of preparation have been published before.[18]

Procedure. All weighing was carried out in a Mettler Toledo AT 261 balance with an uncertainty of ± 10^{-4} g. Water contents were measured using a Karl Fischer titration method in a 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 ± $4·10^{-5}$.

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. Previous experiments showed that equilibrium was established after about 2 h of stirring to get a good contact between both phases and overnight to settle down. Then, samples of both layers were withdrawn using syringes, and thiophene and methylcyclohexane compositions were analyzed by gas chromatography (GC) using an internal standard method. IL composition was calculated by difference. The GC used was an HP 6890 series equipped with a thermal conductivity detector (TCD), an HP-FFAP Polyethylene Glycol TPA (25 m × 200 μm × 0.3 μm) capillary column, and an empty precolumn to protect the column and collect the ionic liquid that could not be retained by the liner. The GC operating conditions are given in Table 2. The estimated uncertainty in the determination of mole fraction compositions is ± 0.006.

Results and Discussion

Experimental LLE Data. The compositions of the experimental tie-lines for 1-methyl-3-octylimidazolium bis[trifluoromethylsulfonyl]imide ([C_8mim][NTf_2]) + thiophene + me-

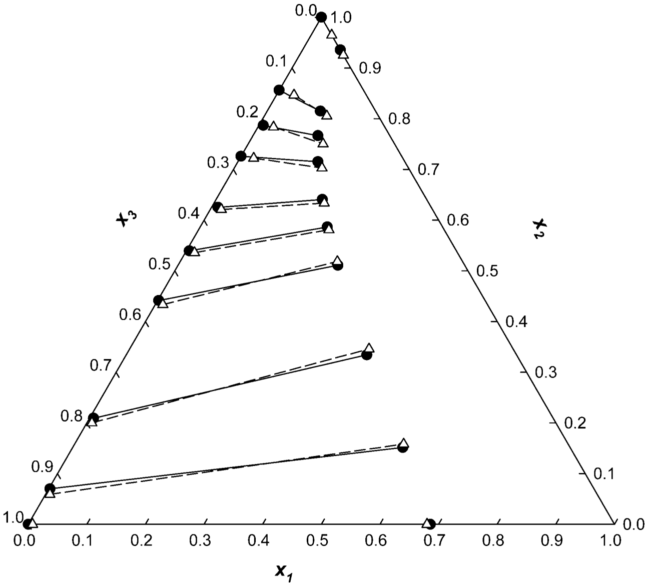

Figure 2. Experimental —●— and NRTL (α = 0.3) - -△- - tie-lines for the LLE of the ternary system {[C$_8$mim][NTf$_2$] (1) + thiophene (2) + methylcyclohexane (3)} at 298.15 K.

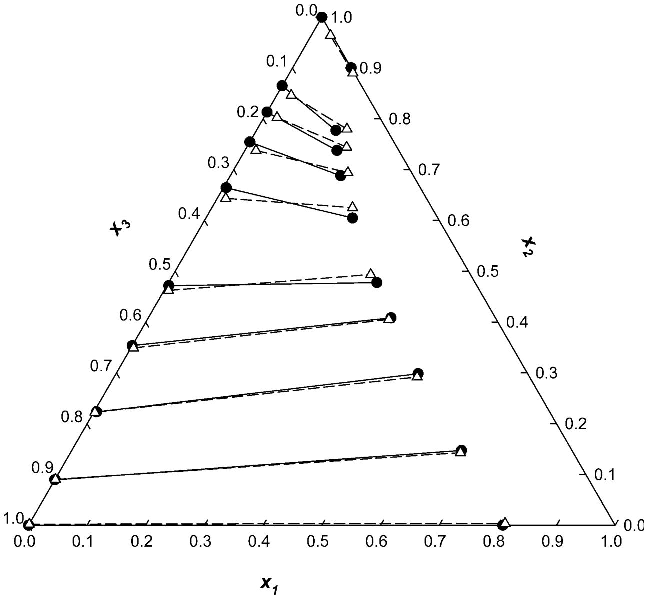

Figure 3. Experimental —●— and NRTL (α = 0.1) - -△- - tie-lines for the LLE of the ternary system {[C$_8$mim][BF$_4$] (1) + thiophene (2) + methylcyclohexane (3)} at 298.15 K.

thylcyclohexane and l-methyl-3-octylimidazolium tetrafluoroborate ([C$_8$mim][BF$_4$]) + thiophene + methylcyclohexane ternary systems at 298.15 K are reported in Tables 3 and 4, respectively. Values of solute distribution ratios β and selectivities S are also shown in those tables. These parameters are defined as follows

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

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

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 2 and 3. Analogously, Figures 4 and 5 show the solute distribution ratios and selectivities plotted against the molar fraction of solute in the hydrocarbon-rich phase.

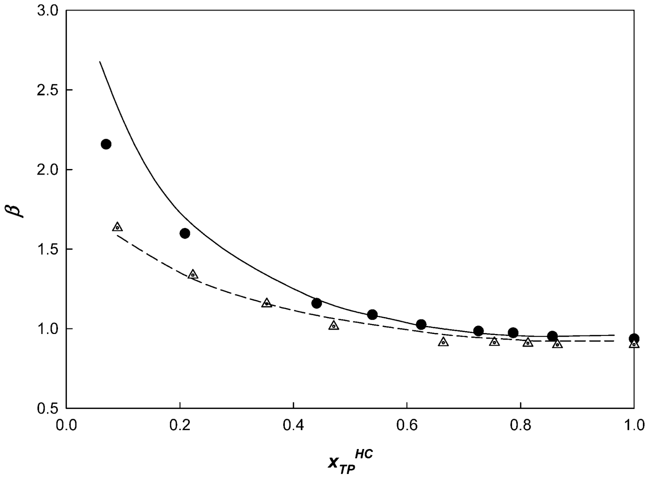

Figure 4. Solute distribution ratio as a function of the mole fraction of solute in the hydrocarbon-rich phase ($x_{\mathrm{TP}}^{\mathrm{HC}}$). ●, β^{exptl} for [C$_8$mim][NTf$_2$]; —, $\beta^{\mathrm{NRTL}(\alpha=0.3)}$ for [C$_8$mim][NTf$_2$]; △, β^{exptl} for [C$_8$mim][BF$_4$]; - - -, $\beta^{\mathrm{NRTL}(\alpha=0.1)}$ for [C$_8$mim][BF$_4$].

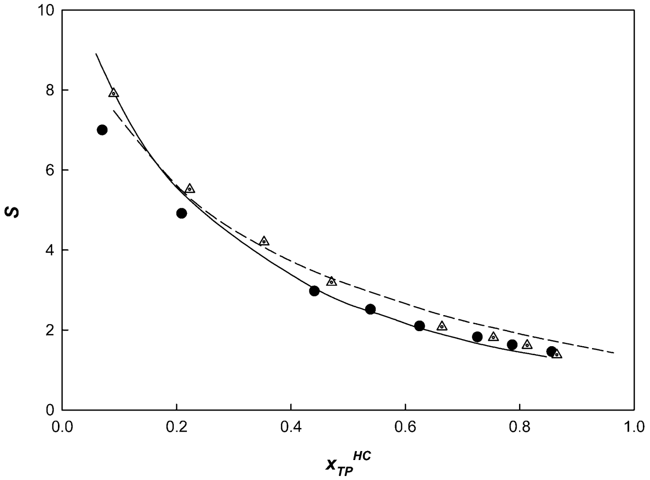

Figure 5. Selectivity as a function of the mole fraction of solute in the hydrocarbon-rich phase ($x_{\mathrm{TP}}^{\mathrm{HC}}$). ●, β^{exptl} for [C$_8$mim][NTf$_2$]; —, $\beta^{\mathrm{NRTL}(\alpha=0.3)}$ for [C$_8$mim][NTf$_2$]; △, β^{exptl} for [C$_8$mim][BF$_4$]; - - -, $\beta^{\mathrm{NRTL}(\alpha=0.1)}$ for [C$_8$-mim][BF$_4$].

Correlation of LLE Data. The correlation of the experimental data was done with the NRTL[5] equation. The value of the nonrandomness parameter, α, was previously assigned as 0.1, 0.2, and 0.3. The binary interaction parameters were obtained using a computer program described by Sϕrensen and Arlt,[19] 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

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

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

where a is the activity and x is the experimental and $\hat{x}$ is the corresponding calculated mole fraction. 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 $\hat{\gamma}^{\mathrm{I}}_{S\infty}$ and $\hat{\gamma}^{\mathrm{II}}_{S\infty}$ 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 all symbols have the same meanings as in eqs 3 and 4 and M refers to the number of experimental tie-lines.

For both systems studied, Tables 5 and 6 show the binary interaction parameters and residuals for correlation. Correlated compositions, distribution ratios, and selectivities were included in Figures 2 to 5 for comparison with experimental values.

Conclusions

Experimental research of the equilibrium behavior of ternary mixtures 1-methyl-3-octylimidazolium bis[trifluoromethylsulfonyl]imide or l-methyl-3-octylimidazolium tetrafluoroborate with thiophene and methylcyclohexane was carried out at a temperature of 298.15 K and atmospheric pressure. The values of the solute distribution ratios and selectivities for both ternary systems have been calculated.

Solubility of thiophene on both ILs is high, being slightly larger in the case of the [C_8mim][NTf_2]. Nonetheless, the solubility of methylcyclohexane is also higher in this IL. The same behavior is found on ternary mixtures. Solute distribution ratios are higher for systems with an ionic liquid containing [NTf_2] cation, but due to the also higher solubility of the cycloalquene in this ionic liquid, selectivities are slightly smaller for this system. In any case, for the two systems studied, solute distribution ratios and selectivities are higher than one at low thiophene concentrations (note that in the desulfurization of fossil fuels the content of sulfur compounds is low, making both ionic liquids potential solvents for the separation of thiophene). A wider study on equilibrium with the other compounds present in the real mixture to desulfurizate is necessary to focus a technological study on one of these ionic liquids.

The experimental LLE data were correlated using the NRTL equation. For the ternary system with [C_8min][NTf_2], the best results were found with $\alpha = 0.3$, and for the ternary system with [C_8min][BF_4], the best results were found with $\alpha = 0.1$. Nonetheless, in both cases, there are significant deviations at high concentrations of solute where the NRTL model does not adequately correlate experimental data.

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