J. Chem. Eng. Data **2000,** *45,* 841−845

Liquid−Liquid Equilibria for Toluene + Heptane + 1-Ethyl-3-methylimidazolium Triiodide and Toluene + Heptane + 1-Butyl-3-methylimidazolium Triiodide†

Murugan S. Selvan, Marvin D. McKinley,* Raymond H. Dubois, and Jerry L. Atwood

Department of Chemical Engineering, The University of Alabama, Tuscaloosa, Alabama 35487

This study focuses on the use of an ionic liquid for extracting an aromatic hydrocarbon from a mixture of an aromatic and an aliphatic hydrocarbon. Liquid−liquid equilibrium data were collected for the toluene + heptane + 1-ethyl-3-methylimidazolium triiodide system at 45 °C and for the toluene + heptane + 1-butyl-3-methylimidazolium triiodide system at 35 °C. The nonrandom two-liquid (NRTL) physical thermodynamic model was used to correlate the experimental data. The NRTL model was found to represent the data very well. The selectivity and capacity of the ionic liquids for extracting toluene from toluene + heptane solutions were evaluated. The separation factors were found to be above 50 for low toluene compositions and nearly unity for high toluene compositions.

Introduction

Physical separation processes have a major economic bearing on the manufacture of chemical products and are an important component of a large fraction of the chemical process industries. Many of the existing processes are complex, involve several process units, and are energy intensive. Interest in the use of ionic liquids to replace volatile solvents in industrial processes has increased greatly in recent years. Development of ionic liquids that are stable in contact with air and water has greatly increased the potential for industrial application (Wilkes and Zaworotko, 1992; Huddleston et al., 1998). Chauvin and Olivier-Bourbigou (1995), Seddon (1997), Olivier (1998), and Welton (1999) review the use of ionic liquids as solvents for organic synthesis and catalysis, which gives promise for clean technology applications. Fuller et al. (1997, 1998) and Carlin et al. (1998) describe applications of ionic liquids in electrochemical operations. Huddleston et al. (1998) describe the use of 1-butyl-3-methylimidazolium hexafluorophosphate as a liquid extraction medium for extracting substituted-benzene derivatives from water.

Most of the research described above makes use of the unique affinity of many ionic liquids for specific types of compounds such as a solvent in chemical reactions. Huddleston et al. (1998) is the only work referenced above in which the use of an ionic liquid for a purely physical process was investigated: liquid extraction. Huddleston's study was a screening study in which partition coefficients were determined for twelve different compounds between an aqueous phase and an ionic liquid phase, but the partition coefficients were not studied as a function of composition. In the present work, phase equilibrium data were measured and correlated in order to investigate whether the preference of ionic liquids for aromatic compounds could be exploited to extract aromatic compounds from mixtures of aromatics and paraffins.

An ionic liquid, owing to its remarkable selectivity toward aromatic hydrocarbons, potentially can be used as an extractive agent to reduce the complexity and high energy cost of existing aromatic/paraffin separation processes. The extracted aromatic hydrocarbon can be reclaimed by temperature reduction of the ionic liquid/aromatic complex by only a few degrees. Although the nature of ionic liquids has been well documented scientifically, little work has been directed toward analysis of the complexes from an engineering standpoint. In particular, the separation factor and extractive capacity of the ionic liquid have not been measured over a wide composition range. The purpose of the present study was to gather experimental liquid−liquid equilibrium data over a wide composition range and correlate the phase compositions using the nonrandom two-liquid (NRTL) model for two systems: the toluene + heptane + 1-ethyl-3-methylimidazolium triiodide system at 45 °C and the toluene + heptane + 1-butyl-3-methylimidazolium triiodide system at 35 °C.

Experimental Section

Materials. The following materials were purchased from Aldrich Chemical Co.: 1-methylimidazole (99+%), iodoethane (99%), iodobutane (99%), tetrahydrofuran (THF, 99+%), acetone (99.5+%, ACS reagent). The following chemicals were purchased from Fisher Scientific: hexane (ACS certified), iodine (USP resublimated crystals), toluene (ACS certified), heptane (ACS certified). The hexane and THF were distilled over anhydrous calcium hydride under nitrogen before use.

The ionic liquids used in this study were prepared by the following procedures:

(1) 1-Ethyl-3-methylimidazolium Triiodide ($EtMeImI_3$). 1-Methylimidazole (5 cm^3, 62.7 mmol) was dissolved in 100 cm^3 of THF, and 5.5 cm^3 (66.8 mmol) of iodoethane was added to the solution in a 250 cm^3 round-bottomed flask. The mixture was refluxed for 20 h with vigorous stirring under a positive pressure of nitrogen. Initially the mixture formed two liquid phases; however, after comple-

---

* To whom correspondence should be addressed. E-mail: mmckinley@coe.eng.ua.edu.

† Taken in part from the Ph.D. dissertation of M. S. Selvan, The University of Alabama.

10.1021/je990231p CCC: $19.00

tion of the reaction period and cooling to room temperature a pale yellow solid was isolated. This solid was filtered and washed with 50 to 100 cm^3 of hexane. The salt was dried under vacuum for 24 h.

A saturated solution of I_2 (1.07 g, 4.20 mmol) in acetone was added to a solution of 1.00 g (4.20 mmol) of the salt prepared above in 75 cm^3 of acetone. The solution was stirred for 10 min at room temperature. The acetone was removed by rotoevaporation, leaving purple-black crystals. These crystals were washed with hexane to remove excess I_2 and then were dried under vacuum for 20 h.

(2) 1-Butyl-3-methylimidazolium Triiodide(BuMeImI$_3$). The same procedure was used, except that iodobutane was substituted for iodoethane.

Phase Equilibrium Equipment. The liquid−liquid equilibrium measurements were made by using a jacketed 40 cm^3 cylindrical glass equilibrium vessel (2.5 cm inside diameter and 8 cm long). The top was closed using a Teflon cover, through which the stirrer shaft passed. A Teflon paddle stirrer was used. The speed of the stirrer was varied using a speed regulator connected to the motor. The ionic liquid phase is viscous, and the paddle stirrer was required because magnetic stirring did not give satisfactory agitation. The vessel was equipped with a water jacket to maintain the desired temperature by circulating water from a bath equipped with a temperature regulator (Fischer-Scientific, model 9000) which is capable of controlling temperature within (±0.05 °C using a digital bridge.

Procedures. For each run, a measured mass or volume of ionic liquid was placed in the cell (6 ± 0.1 g if the salt was solid or 5 ± 0.1 cm^3 of liquid at room temperature if the salt was liquid). The cell was initially held at a desired temperature and was dry before the ionic liquid was added. Proportional volumes of toluene and heptane to add up to 10 cm^3 were added (e.g. 9 cm^3 of toluene + 1 cm^3 of heptane) for each batch of ionic liquid. The mixture was stirred for at least 2 to 3 h to reach equilibrium, the agitation was stopped, and the two liquid phases were allowed to settle until no droplets were visible in either phase. Two samples (3 cm^3 each) of the two phases were withdrawn for analysis by glass syringes equipped with stainless steel hypodermic needles and then stored in closed glass vials in an air bath to await chemical analysis. Particular attention was paid to sampling operations; the syringe was heated to the same temperature as the liquid mixture in the equilibrium cell to avoid phase splitting during sampling.

Analysis. Because the ionic liquid does not elute from a gas chromatograph, analysis of the ionic liquid phase (extract phase) requires both nuclear magnet resonance (NMR) (^{1}H NMR, 60 MHz and 200 MHz) and GC analysis to determine the composition of the three-component mixture. NMR spectra were run for the samples of the lower (ionic liquid) phase to provide the ratio of toluene to ionic liquid, thereby giving the amount of toluene contained in that phase. The NMR instrument was operated at a higher temperature than that at which the sample was taken in order to prevent phase separation during the analysis. The NMR spectra did not give an accurate hexane content, so GC was used to determine the ratio of heptane to toluene. Combination of these two analyses allowed calculation of the composition of the ionic liquid phase. The ionic liquid is nonvolatile, and in order to prevent fouling or contamination of the primary column with solid, a precolumn packed with silica was used. The injection port was cleaned before analysis of a sample containing a different ionic liquid than the previous sample by swabbing with a cotton swab wet with a mixture of acetone and water.

Table 1. Tie-Line Data for the Toluene (1) + Heptane (2) + 1-Ethyl-3-methylimidazolium Triiodide (3) System at 45 °C in Mole Fractions (rmsd = 0.0145)

ionic liquid phase			organic phase		
x_3'	x_1'	x_2'	x_3''	x_1''	x_2''
0.922	0.063	0.016	0.00	0.075	0.925
0.909	0.067	0.024	0.00	0.053	0.947
0.913	0.075	0.012	0.00	0.085	0.915
0.895	0.079	0.026	0.00	0.064	0.936
0.891	0.093	0.016	0.00	0.090	0.910
0.593	0.370	0.037	0.00	0.170	0.830
0.498	0.476	0.026	0.00	0.370	0.630
0.451	0.523	0.026	0.00	0.470	0.530
0.417	0.552	0.031	0.00	0.595	0.415
0.377	0.595	0.028	0.00	0.700	0.300
0.341	0.626	0.033	0.00	0.790	0.210
0.317	0.654	0.029	0.00	0.880	0.120
0.312	0.660	0.028	0.00	0.915	0.085
0.293	0.707	0.000	0.00	1.000	0.000

Table 2. Tie-Line Data for the Toluene (1) + Heptane (2) + 1-Butyl-3-methylimidazolium Triiodide (3) System at 35 °C in Mole Fractions (rmsd = 0.00892)

ionic liquid phase			organic phase		
x_3'	x_1'	x_2'	x_3''	x_1''	x_2''
0.616	0.332	0.052	0.00	0.055	0.945
0.541	0.395	0.064	0.00	0.170	0.830
0.509	0.436	0.055	0.00	0.275	0.725
0.441	0.503	0.056	0.00	0.365	0.635
0.390	0.549	0.061	0.00	0.465	0.535
0.385	0.553	0.061	0.00	0.480	0.520
0.362	0.583	0.055	0.00	0.590	0.410
0.319	0.620	0.061	0.00	0.675	0.325
0.289	0.661	0.049	0.00	0.765	0.235
0.259	0.695	0.045	0.00	0.870	0.130
0.223	0.777	0.000	0.00	1.000	0.000

The gas chromatograph used was an HP 5830A, equipped with a flame ionization detector and a compatible integrator, model HP 18850A. The capillary column of 30 m × 0.32 mm i.d., charged with carbowax, was used with helium as the carrier gas. The septum was changed for each new sample. To precondition the column, methanol was injected and allowed to elute before a sample was injected for analysis. The gas chromatograph was calibrated by injecting eight different mixtures of known composition prepared gravimetrically and by using these data to prepare a calibration curve of area percent versus mole fraction.

There was no detectable ionic liquid in the organic phase (raffinate), so only the GC was required for analysis of the upper organic phase. The precision of the composition measurements was considered to be ±0.001 in mole fractions for the ionic liquid + toluene + heptane system. For each sample two analyses were performed to obtain an average value.

Results and Discussion

Experimental Data. The experimental tie-line data for the toluene + heptane + 1-ethyl-3-methylimidazolium triiodide and the toluene + heptane + 1-butyl-3-methylimidazolium triiodide systems are presented in Tables 1 and 2, respectively. The equilibrium data for low concentrations of toluene are of special interest and were studied in some detail for the first system, as presented in Table 1. Figures 1 and 2 present the ternary diagrams representing the experimental data.

Separation Factor. The separation factor for separating toluene and heptane, α_s, is defined in terms of mole

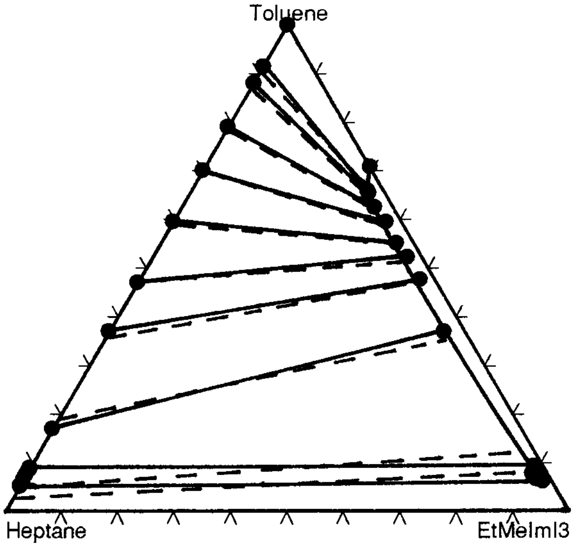

Figure 1. Liquid–liquid equilibrium for the system toluene + heptane + 1-ethyl-3-methylimiazolium triiodide (EtMeImI$_3$) at 318.2 K (45 °C). [Key: ●, experimental data; —, experimental tie line; – – –, calculated tie line from the NRTL equation.]

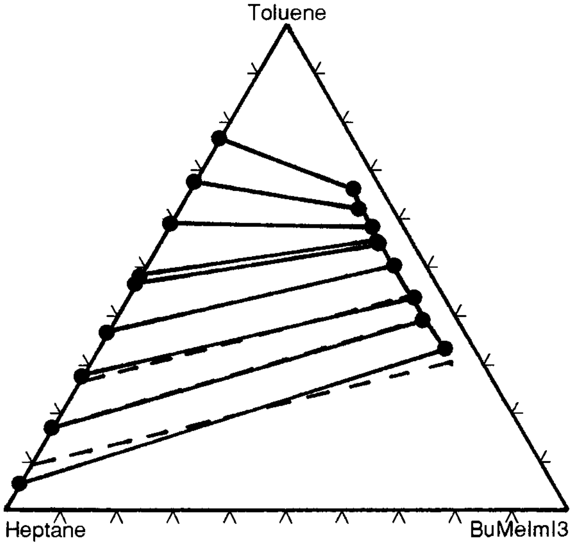

Figure 2. Liquid–liquid equilibrium for the system toluene + heptane + 1-butyl-3-methylimiazolium triiodide (BuMeImI$_3$) at 308.2 K (35 °C). [Key: ●, experimental data, —, experimental tie line, – – –, calculated tie line from the NRTL equation.]

fractions as shown below

$$\alpha_s = (x_1'/x_1'')/(x_2'/x_2'') \quad (1)$$

where x is mole fraction, subscript 1 is toluene, subscript 2 is heptane, ′ represents the ionic liquid phase, and ″ represents the organic phase. Figure 3 presents the separation factor data. The selectivity or separation factor is observed to have an exponential dependence on the toluene compositions. Figure 3 shows that at low toluene concentrations separation factors are very high (on the order of 50 or above) as compared to those of other traditional solvents whose selectivities are much lower. At higher concentrations of toluene the separation factors tend toward unity, indicating that it would be difficult to regenerate pure aromatic hydrocarbons from the ionic liquid. However, the ionic liquid should be able to remove most of the toluene from heptane, leaving a high-purity sample of heptane.

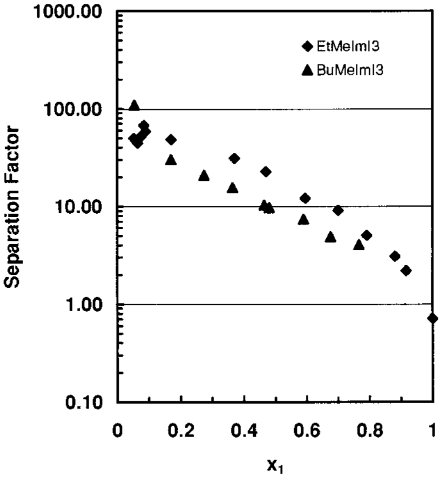

Figure 3. Variation of the separation factor with toluene mole fraction in the organic phase.

Hydrocarbon Solubility. The hydrocarbon solubility, α (ratio of moles of hydrocarbons to the moles of ionic liquid), represents the total hydrocarbons trapped by the ionic liquid and is defined as follows:

$$\alpha = (x_1' + x_2')/x_3' \quad (2)$$

where x_3' is the mole fraction of ionic liquid. The solubilities varied linearly with toluene mole fraction in the organic phase. When in contact with pure toluene, the ionic liquid phase contains about 2.4 mol of toluene per mole of ionic liquid for EtMeImI$_3$, and for BuMeImI$_3$ the ionic liquid phase contains about 3.5 mol of toluene per mole of ionic liquid. For low mole fractions of toluene in the organic phase, the solubility becomes very low, approaching zero in the limit of no toluene, as expected. Although the solubility of organics in the ionic liquid is low for low toluene mole fractions, the separation factor becomes very large. The overall effect is that the ionic liquid is an effective solvent for removing toluene from hexane that contains only a small amount of toluene.

Thermodynamic Models and Data Correlation

Thermodynamic models such as the van Laar (1910), Wilson (1964), universal quasi-chemical (UNIQUAC) (1975), and universal quasi-chemical functional group activity coefficient (UNIFAC) (1977) models have historically been used to explain the physical and, sometimes, the chemical interactions in solutions. They have been consistently applied to correlate the phase equilibria data for numerous solvents. The van Laar and Wilson models failed to satisfactorily correlate the phase compositions for the present nonideal systems. In particular, the original Wilson model cannot describe liquid–liquid equilibria. The UNIFAC equations are based on group contributions, and while the parameters are available for toluene and heptane, the molecular parameters are not available for the ionic liquids and would require determination from experimental data. The UNIFAC equations do not work as well for liquid–liquid equilibria as they do for vapor–liquid equilibria, so this method was not pursued. The UNIQUAC method involves molecular parameters for the pure compounds as well as binary parameters for each binary pair in the system. Again, molecular parameters are available for toluene and heptane, but the parameters for the ionic liquids would have to be determined. To fit the data using UNIQUAC would require the evaluation of eight parameters. The lack of the ionic liquid's acentric factor, dipole moment, polarizability, and critical properties makes the use of other available theories such as lattice theory difficult. It was felt that the NRTL model was the best alternative for fitting the phase equilibrium data.

Nonrandom Two-Liquid Model

The nonrandom two-liquid (NRTL) model developed by Renon and Prausnitz (1968) gives the following equations for representing liquid-phase activity coefficients:

$$\ln \gamma_i = \frac{\sum_{j=1}^{m} x_j \tau_{ji} G_{ji}}{\sum_{k=1}^{m} x_k G_{ki}} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{k=1}^{m} x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{r=1}^{m} x_r G_{rj} \tau_{rj}}{\sum_{k=1}^{m} x_k G_{kj}} \right) \qquad (3)$$

where:

$$\tau_{ij} = \frac{(g_{ij} - g_{jj})}{RT}; \quad G_{ij} = \exp(-\alpha_{ij}\tau_{ij}); \quad (\alpha_{ij} = \alpha_{ji}) \qquad (4)$$

where g = the energy parameter, x = the mole fraction, α_{ij} = the nonrandomness parameter, γ = the activity coefficient, τ = the interaction parameter, and i, j, k = the component indices. The present liquid−liquid system, that is, toluene (1) + heptane (2) + 1-ethyl-3-methylimidazolium triiodide (3), requires that six binary interaction parameters be evaluated. In this system, components 1 and 2 are completely miscible but components 1 and 3 and 2 and 3 are only partially miscible.

Program to Estimate Binary Interaction Parameters

To calculate phase compositions for a ternary mixture, it is essential to estimate binary parameters for each of the three binaries that constitute the ternary system before beginning the regression to determine the optimum set of parameters. Data for the toluene + heptane system are available and were used as first estimates to begin the computations. For 1-ethyl-3-methylimidazolium triiodide + toluene + heptane, no binary data exist in order to provide initial estimates of the parameters. To start the regression analysis, the initial NRTL parameters for the ionic liquid + toluene and ionic liquid + heptane binary solutions were estimates based upon typical values for other compounds. If the regression failed to converge, a different set of parameters was used.

To obtain a set of parameters that can be used to represent all the experimental tie lines in the phase equilibrium data set, parameters for all of the binary pairs are optimized together. The inherent limitation in all optimization codes is that there is no unique set of parameters which gives accurate predictions. Regardless of how abundant the data, and how suitable the model for G^E, excess free energy, there is always some uncertainty in the binary parameters (Prausnitz, 1986). Therefore, it is not possible to specify a unique set of binary parameters. The best set of parameters are determined by minimizing an objective function, OBFN, defined in terms of the concentrations as given by the following expression.

$$\mathrm{OBFN} = \sum_{k=1}^{n} \sum_{i=1}^{3} \sum_{j=1}^{2} \left[\frac{(x_{ijk}(\mathrm{exptl}) - x_{ijk}(\mathrm{calcd}))^2}{6n} \right]^{1/2} \qquad (5)$$

Table 3. NRTL Parameters for the Ternary Systems Investigated

$i + j$	τ_{ij}	τ_{ji}
toluene + heptane	1.7295	−0.11356
toluene + $\mathrm{EtMeImI_3}$	7.5823	−0.96606
heptane + $\mathrm{EtMeImI_3}$	6.3906	7.3175
toluene + heptane	1.0090	0.37426
toluene + $\mathrm{BuMeImI_3}$	7.0048	−1.4132
heptane + $\mathrm{BuMeImI_3}$	6.5496	6.6332

An iterative computer program written in BASIC (Arnold, 1991) was used to correlate experimental phase equilibria (tie-line) data by using the NRTL method. The parameter optimization was done using a Nelder-Mead simplex method (Wilson, 1986). The set of parameters determined by regression analysis normally depends on the parameter estimates to start the computation. Once convergence was obtained, several sets of parameters with values close to the values determined by the regression analysis were used to restart the analysis. The set of parameters that gave the best fit was accepted.

For the present system, the nonrandomness parameter is set at $\alpha = 0.30$. Generally, α depends on the molecular properties (e.g. the potential for forming hydrogen bonds) and is independent of temperature. According to Renon and Prausnitz (1968), and Silverman et al. (1977), $\alpha = 0.30$ can be chosen for mixtures of nonpolar and polar nonassociated species (e.g. toluene−ionic liquid). This value for α is used to provide improved correlation of the data and was not adjusted in developing the correlation. The six adjustable interaction parameters τ_{12}, τ_{21}, τ_{23}, τ_{32}, τ_{13}, and τ_{31} were determined using the computer code. Note that the remaining three parameters τ_{11}, τ_{22}, and τ_{33} are set equal to zero because they represent intramolecular interactions.

Figures 1 and 2 show both the experimental tie lines and the tie lines calculated using the NRTL equation and the six parameters determined here. There is very good agreement between calculation and experiment for high toluene mole fractions (above 20 mol % in the ionic liquid phase), but the deviations become greater at low toluene mole fractions. Table 3 gives the set of six interaction parameters needed for calculating the phase compositions for each ionic liquid system studied.

The root-mean-square deviation is calculated from the difference between the experimental and the calculated data according to the following formula:

$$\mathrm{RMSD} = \{\sum_{k}[\sum_{j}(\sum_{i}(x_{i,exp} - x_{i,\mathrm{calcd}})^2)/6n]\}^{1/2} \qquad (6)$$

where i is toluene or heptane, j is the organic or ionic liquid phase, and k = 1, 2, ..., n tie lines. The rmsd's are given in Tables 1 and 2. The calculated numerical values of the binary interaction parameters for the ionic liquid system ($\mathrm{BuMeImI_3}$) are close to those of the system ($\mathrm{EtMeImI_3}$), despite their different molecular sizes.

Conclusions

The focus of the study was to measure liquid−liquid equilibrium data and to determine the separation factor and the hydrocarbon solubility in the ionic liquid. The suitability of the various existing thermodynamic models was also investigated in order to correlate the highly nonideal behavior of the two ionic liquid systems ($\mathrm{EtMeImI_3}$ and $\mathrm{BuMeImI_3}$) with a mixture of toluene and heptane.

The nonrandom two-liquid model represents the ternary systems quite well, and the predicted data can be useful for process design. The present work not only provides reliable binary interaction parameters but also establishes the applicability of the NRTL thermodynamic model, which had not previously been applied to such a complex solvent system.

Literature Cited

Abrams, D. S.; Prausnitz J. M. Statistical Thermodynamics of liquid mixtures; a new expression for the excess Gibbs energy of partly or completely miscible systems. *AICHE J.* **1975**, *21*, 116−128.

Arnold, D. W. Advanced Thermodynamics I & II—course notes, The University of Alabama, 1991.

Carlin, R. T.; De Long, H. C.; Fuller, J.; Trulove, P. C. Microelectrode evaluation of transition metal-aluminum alloy electrodepositions in chloroaluminate ionic liquids. *J. Electrochem. Soc.* **1998**, *145* (5), 1598−1607.

Chauvin, Y.; Olivier-Bourbigou, H. Nonaqueous ionic liquids as reaction solvents. *Chemtech* **1995**, *25* (9), 26−30.

Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor−Liquid Equilibrium Using UNIFAC*; Elsevier: Amsterdam, 1977.

Fuller, J.; Carlin, R. T. Anodization of light metals in chloride rich room-temperature ionic liquids. *Proc. Electrochem. Soc.* **1997**, *97-13*, 218−226.

Fuller, J.; Carlin, R. T.; Osteryond, R. A.; Koranaios, P.; Mantz, R. Anodization and speciation of magnesium in chloride-rich room-temperature ionic liquids. *J. Electrochem. Soc.* **1998**, *145* (1), 24−28.

Huddleston, J. G.; Willauer, H. D.; Swatlski, R. P.; Visser, A. E.; Rogers, R. D. Room temperatue ionic liquids as novel media for “clean” liquid−liquid extraction. *Chem. Commun.* **1998**, *16*, 1765−1766.

Olivier, H. Nonaqueious ionic liquids. In *Aqueous-Phase Organometallic Catalysis*; Cornils, B., Herrmann, W. A., Eds.; Wiley−VCH Verlag GmbH: Weinheim, Germany, 1998; pp 555−563.

Prausnitz, J. M.; Lichtenthaler, R. N.; Gomes de Azevedo, E. *Molecular Thermodynamics of Fluid Phase Equilibria*, 2nd ed.; Prentice Hall Inc.: Englewood Cliffs, NJ, 1986; Appendix V.

Renon, H.; Prausnitz, J. M. Local composition in thermodynamic excess functions for liquid mixtures. *AICHE J.* **1968**, *14*, 135−144.

Seddon, K. R. Ionic liquids for clean technology. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351−356.

Silverman, N.; Tassios, D. The number of roots in the Wilson equation and its effect on vapor-liquid equilibrium calculations. *Ind. Eng. Chem. Process Des. Dev.* **1977**, *16*, 13−20.

van Laar, J. J. The vapor pressure of binary mixtures. *Z. Phys. Chem.* **1910**, *72*, 723−751.

Welton, T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.* **1999**, *99*, 2071−2083.

Wilkes, J. S.; Zaworotko, M. J. Air and water stable 1-ethyl-3-methylimizaolium based ionic liquids. *J. Chem. Soc., Chem. Commun.* **1992**, *12*, 965−967.

Wilson, G. M. Vapor-liquid equilibrium. XI. A new expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.

Wilson, H. B. Optimization of parameters using the Nelder−Mead simplex method. Personal communications, The University of Alabama, 1986.

Received for review August 18, 1999. Accepted May 26, 2000. The authors wish to thank the National Science Foundation for their generous support of this research through Contract No. 30781.

JE990231P