514 *J. Chem. Eng. Data* **2004,** *49,* 514−517

Experimental Determination of Liquid−Liquid Equilibrium Using Ionic Liquids: *tert*-Amyl Ethyl Ether + Ethanol + 1-Octyl-3-Methylimidazolium Chloride System at 298.15 K

Alberto Arce,* Oscar Rodríguez, and Ana Soto

Department of Chemical Engineering, University of Santiago de Compostela, Lope Gómez de Marzoa, s/n. E-15782 Santiago de Compostela, Spain

---

Liquid−liquid equilibrium data for *tert*-amyl ethyl ether (TAEE) + ethanol + 1-octyl-3-methylimidazolium chloride were measured experimentally at 298.15 K. The experimental data were obtained by direct analysis of phases at equilibrium by ^{1}H NMR and then correlated using the nonrandom two-liquid equation. The nonrandomness parameter (α) was fixed to 0.1, 0.2, and 0.3, and the best results were found with $\alpha = 0.1$. Distribution coefficients and selectivities obtained show that the ionic liquid used can be an excellent extractant agent of ethanol from its mixtures with TAEE, thus allowing ether purification.

---

1. Introduction

Room-temperature ionic liquids (RTIL) are ionic compounds whose melting point is 100 °C or below. Over the past few years, research concerning RTIL has grown greatly, as can be seen in the scientific literature. There is an increasing number of articles reporting new applications and thermophysical properties for pure RTIL and their mixtures. These applications are mainly as new solvents because of their properties:[1,2]

(1) RTIL have negligible vapor pressure, so atmospheric contamination is avoided, and thus the RTIL are more benign compounds for the environment than organic solvents.

(2) Many different cations and anions can be used to synthesize the RTIL, so the RTIL properties can be “designed” by use of different, selected combinations of anions and cations, the so-called “designer solvents”.

(3) They have a wide liquid range, which allows for better kinetic control on reactions.

Most applications of RTIL[2,3] are as solvents carrying out different reactions, including biocatalyzed or homogeneously catalyzed reactions, gas separations, liquid extraction, electrolytes, or heat-transfer fluids.

Articles intended for liquid extraction applications report mainly liquid−liquid equilibrium (LLE) data for binary systems or distribution ratios for several compounds (that is, the ratio of solubilities of the compound between two immiscible solvents, one of which is a RTIL).[4−11] Only a few works have been published with LLE data for a ternary system,[12−14] despite its practical importance in chemical engineering for extraction equipment design.

This work reports the experimental tie lines for the ternary system *tert*-amyl ethyl ether (TAEE) + ethanol + 1-octyl-3-methyl-imidazolium chloride (OMImCl) at 298.15 K. TAEE can be used as an octane booster on gasoline blending, substituting to methyl *tert*-butyl ether (MTBE). Ethanol is used in excess on the TAEE production, and it usually involves an extraction unit to separate the mixture of TAEE + ethanol. Thus, the system studied would be of interest for the TAEE production unit, as there are no data in the literature for the mixture reported.

2. Experimental Section

Materials. TAEE was supplied by the Yarsintez Research Institute (Yaroslav, Russia) with a nominal purity of 99.8 mass %. Ethanol was supplied by Merck with a nominal purity of 99.8 mass %. OMImCl was supplied by Fluka with a nominal purity of 97 mass %. These purities were verified by gas chromatography (for TAEE and ethanol) and ^{1}H NMR (for OMImCl), and the chemicals were used without further purification. The water content of TAEE, ethanol, and OMImCl was 0.04, 0.05, and 0.15 mass %, respectively. Table 1 lists the compounds used, CAS register number, water content, and the experimental and published values[15−17] of densities (ρ), refractive indices (n_D), and speeds of sound (u).

Procedure. All weighing was carried out in a Mettler Toledo AT 261 balance precise to within $\pm 10^{-4}$ g. Water content was measured with a Metrohm 737 KF coulometer. Densities of TAEE and ethanol were measured with an Anton Paar DMA 60/602 densimeter, with a precision of $\pm 10^{-5}$ g·cm^{-3}. Density of OMImCl and speeds of sound for the three components were measured using an Anton Paar DSA 48, with a precision of $\pm 10^{-4}$ g·cm^{-3} in densities and ±1 m/s in speeds of sound. Refractive indices were measured with an Atago RX-5000 refractometer precise to within $\pm 4 \times 10^{-5}$.

Compositions were determined using ^{1}H NMR spectroscopy with a Varian Inova 750 of 17.61 T (^{1}H resonance, 750 MHz). The samples were placed on screw-cap Wilmad tubes (Royal Imperial grade), with PTFE/silicone septa to avoid losses by vaporization. The deuterated solvent used was benzene (C_6D_6, 99.95 atom % D), supplied by Aldrich and selected for its suitable peak. Benzene was not mixed with the sample but added inside a sealed, capillary tube to the NMR tube. Figure 1 shows a typical NMR spectrum of the ternary system, the structure of the molecules, and the correspondence between the hydrogen positions and peaks. The only peaks of TAEE and ethanol suitable for

---

* To whom correspondence may be addressed. E-mail: eqaaarce@usc.es. Fax: 00 34 981 528 050.

10.1021/je0302147 CCC: $27.50

Table 1. CAS Register Number, Water Content (Mass %), Density (ρ), Refractive Indices (n_D), and Speeds of Sound (u) of the Pure Components at 298.15 K and Atmospheric Pressure

			ρ/g·cm^{-3}		n_D		u/m·s^{-1}	
component	CAS no.	mass % water	exp	lit	exp	lit	exp	lit
OMImCl	64697−40−1	0.15	1.0070	1.00[15]	1.50580	1.505[15]	1382	not found
Ethanol	64−17−5	0.05	0.78522	0.78493[16]	1.35920	1.35941[16]	1143	1145[17]
TAEE	919−94−8	0.04	0.76050	not found	1.38857	not found	1096	not found

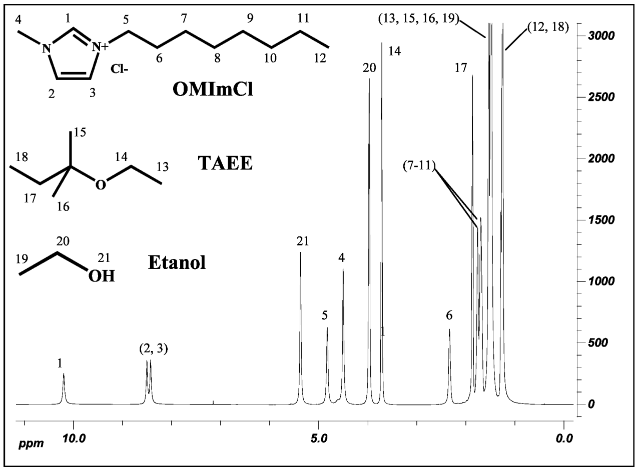

Figure 1. Typical NMR spectrum of a ternary mixture, structure of the molecules, and peak assignment.

integration were peak 14 for ethanol and peak 20 for TAEE (see Figure 1). The peaks are very close; thus a spectrometer of 17.61 T was needed for quantitative integration of these peaks. Peaks 2 and 3 were used together for OMImCl. As the peaks correspond to two hydrogens each, so the component molar fraction is equal to its peak area fraction. First, the technique was tested quantitatively: Samples of known composition were prepared by mass using a Mettler Toledo AT261 (precise to within ±10^{-4} g) and were analyzed on the ^{1}H NMR spectrometer. The largest deviation on mole composition was 0.004.

Mixtures lying on the immiscible region were prepared on jacketed cells with septum outlets. These mixtures were vigorously stirred for at least 2 h, thereafter leaving them to stand overnight to attain equilibrium, for at least 12 h. The temperature was controlled by circulating water from a thermostat (Selecta Ultraterm 6000383), and the water temperature was measured with a thermometer Heraeus Quat 100 precise to within ±0.01 K. Finally a sample of each phase was withdrawn with a syringe and introduced on the NMR tube together with a capillary tube filled with deuterated benzene.

3. Results

The compositions of the ends of the experimental tie lines are reported in Table 2. The experimental tie lines are also presented in Figure 2. The ability of the RTIL OMImCl to separate the TAEE + ethanol mixture is indicated by both the solute-distribution ratio, β, and the selectivity,[18] S, defined as

$$\beta = (x_{\mathrm{EtOH}})^{\mathrm{OM\ Im\ Cl}}/(x_{\mathrm{EtOH}})^{\mathrm{TAEE}} \tag{1}$$

$$S = [(x_{\mathrm{EtOH}})^{\mathrm{OM\ Im\ Cl}}/(x_{\mathrm{TAEE}})^{\mathrm{OM\ Im\ Cl}}]/[(x_{\mathrm{EtOH}})^{\mathrm{TAEE}}/(x_{\mathrm{TAEE}})^{\mathrm{TAEE}}] \tag{2}$$

where x is the molar fraction composition of the compound shown in the subindex, in the phase referred to in the superindex. The values of both β and S are also reported in Table 2. Figure 3 shows the selectivity, S, as a function of ethanol composition on the TAEE-rich phase (the organic phase).

Table 2. Experimental Tie Lines of the System TAEE (x_1) + Ethanol (x_2) + 1-Octyl-3-methylimidazolium Chloride (1 − x_1 − x_2), Solute-Distribution Ratio (β), and Selectivity (S) at 298.15 K[a]

organic phase		ionic liquid phase			
x_1	x_2	x_1	x_2	β	S
0.9997	0.0000	0.0831	0.0000		
0.9967	0.0030	0.1299	0.1183	39.4	302.6
0.9879	0.0119	0.1504	0.2213	18.6	122.2
0.9898	0.0097	0.1707	0.3032	31.2	181.2
0.9895	0.0102	0.1817	0.3277	32.1	175.0
0.9864	0.0133	0.2025	0.3417	25.7	125.1
0.9869	0.0128	0.2104	0.3590	28.0	131.6
0.9802	0.0195	0.2256	0.4109	21.1	91.6
0.9574	0.0421	0.2435	0.4552	10.8	42.5
0.9227	0.0737	0.3110	0.4768	6.5	19.2
0.8998	0.0945	0.4040	0.4517	4.8	10.6

[a] Compositions are in mole fractions.

The correlation of the experimental data was made with the nonrandom two-liquid (NRTL) equation.[19] Despite the fact it is intended for nonelectrolyte solutions, a proper model for RTIL has not yet been developed either for correlation or for prediction purposes. Previous works used the NRTL equation to satisfactorily correlate LLE data.[12−14] The nonrandomness parameter α was previously assigned to 0.1, 0.2, and 0.3. The binary interaction parameters were obtained using the program described by Sϕrensen[20] which uses two objective functions. F_a is used first as it does not require any previous guess for parameters, and after convergence, those parameters are used as initial values in the second function to fit the experimental concentrations, F_b

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

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

where a is the activity, P_n the parameter value, Q a constant, x the composition in mole fraction, $\hat{\gamma}$ the calculated activity coefficient, β the solute-distribution ratio between the organic and the ionic liquid phases (x_2^{TAEE}/$x_2^{\mathrm{OMIm+Cl-}}$), and *min* the minimum obtained by the Marquardt method. The subscripts and superscripts are i for the components (1, 2, 3), j for the phases (I, II), k for the tie lines (1, 2, ..., M), and n for the parameters (1, 2, ...). The symbol ^ refers to calculated magnitudes, s to the solute (ethanol), and ∞ to infinite dilution.

The second terms of both eqs 1 and 2 are penalty terms designed to reduce risks of multiple solutions associated with high parameter values. In F_b, the objective function (eq 3), the third term ensures that the binary interaction

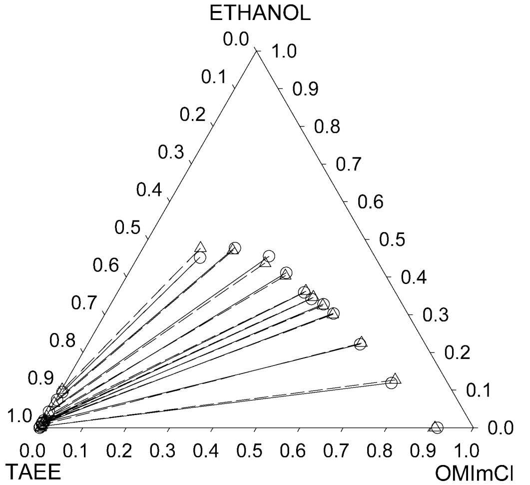

Figure 2. Experimental tie lines (—○) and the corresponding NRTL ($\alpha = 0.1$) correlation (− −△) using the optimal value of the solute-distribution ratio at infinite dilution for the system TAEE + ethanol + OMImCl at 298.15 K.

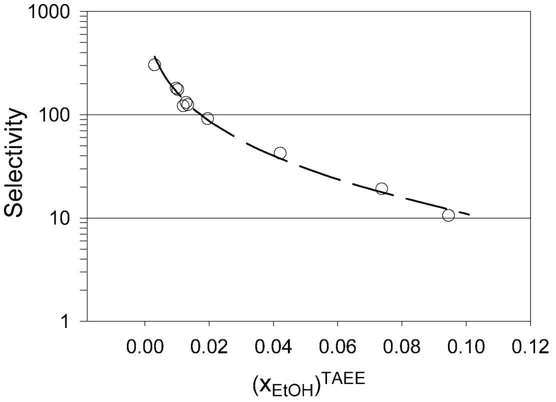

Figure 3. Selectivity, S, as a function of ethanol composition on the organic phase $(x_{EtOH})^{TAEE}$. Experimental values (○) and those calculated with NRTL ($\alpha = 0.1$) using the optimal value of the solute-distribution ratio at infinite dilution (dashed line).

parameters give a solute-distribution ratio at infinite dilution, β_∞, which approximates to a value previously defined by the user.

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

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

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

Data correlation was carried out with each value of the nonrandomness parameter α without defining a value for the solute-distribution ratio at infinite dilution, β_∞, and then the optimal value for β_∞ was found by trial and error with $\Delta\beta$ as the optimality criterion. As is usually found, when β_∞ is fixed at its optimal value, the residual function F slightly increases but $\Delta\beta$ decreases extensively.[21]

The parameters and residuals for this correlation are presented in Table 3. For a best comprehension, Figure 2 shows both the experimental and correlated tie lines in a triangular diagram. The calculated tie lines correspond to NRTL equation with $\alpha = 0.1$ and fixing β_∞ at its optimum.

Table 3. LLE Data Correlation: Binary Interaction Parameters, Root-Mean-Square Deviations (RMSD) for NRTL ($\alpha = 0.1$), Defining or Not the Solute-Distribution Ratio at Infinite Dilution, β_∞

	RMSD (%)	component	Δg_{ij}/J·mol^{-1}	Δg_{ji}/J·mol^{-1}
		OmimCl−EtOH	−773.92	−230.29
$\Delta\beta$	24.6	OmimCl−TAEE	−198.19	1772.5
F	0.6722	EtOH−TAEE	−747.15	1529.1
β_∞	63.13	OmimCl−EtOH	−928.38	381.47
$\Delta\beta$	14.1	OmimCl−TAEE	−256.68	2060.2
F	0.7068	EtOH−TAEE	−745.67	1570.30

4. Conclusions

LLE data of the system TAEE + ethanol + OMImCl were determined experimentally at 298.15 K. The size of the two-phase region is significantly large, indicating the high immiscibility of the pair TAEE + OMImCl (see Figure 2). The slope of the tie lines and the high values obtained for the solute-distribution ratio and selectivity indicate that OMImCl can efficiently extract ethanol from the mixture TAEE + ethanol (see Figure 3). Nevertheless, the selectivity decreases significantly when the ethanol composition increases, which restrains operation to the low ethanol region.

Industrially, ether purification is carried out using water as the extraction solvent. LLE data for TAEE + ethanol + water have been previously reported,[22] but the tie lines lie down toward TAEE. Thus, the solute-distribution ratio is nonfavorable for water, and so this ionic liquid seems a promising alternative for the actual purification process.

The LLE data were correlated using the NRTL activity model. A high number of model parameters leads to an adequate correlation; nonetheless, a new research line must be focused on the RTIL phase equilibria.

The best correlation was found by using NRTL with $\alpha = 0.1$ and by fixing an optimal β_∞ value; in this way, a slightly larger value of the residual F than the correlation without defining β_∞ was found; however, the value of the residual $\Delta\beta$ is much smaller (see Table 3). The same behavior is frequently found in open literature.

Literature Cited

(1) Seddon, K. R. Ionic Liquids for Clean Technology. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351−356.

(2) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, 2003.

(3) Brennecke, J. F.; Maginn, E. J. Ionic Liquids: Innovative Fluids for Chemical Processing. *AIChE J.* **2001**, *47* (11), 2384−2389.

(4) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. Room-Temperature Ionic Liquids as Novel Media for "Clean" Liquid−Liquid Extraction. *Chem. Commun.* **1998**, 1765−1766.

(5) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. Solution Thermodynamics of Imidazolium-Based Ionic Liquids and Water. *J. Phys. Chem. B* **2001**, *105*, 10942−10949.

(6) Fadeev, A. G.; Meagher, M. M. Opportunities for Ionic Liquids in Recovery of Biofuels. *Chem. Commun.* **2001**, 295−296.

(7) Visser, A. E.; Reichert, W. M.; Swatloski, R. P.; Willauer, H. D.; Huddleston, J. G.; Rogers, R. D. Characterization of Hydrophilic and Hydrophobic Ionic Liquids: Alternatives to Volatile Organic Compounds for Liquid−Liquid Separations. *ACS Symp. Ser.* **2002**, *818*, 289−308.

(8) Wong, D. S. H.; Chen, J. P.; Chang, J. M.; Chou, C. H. Phase Equilibria of Water and Ionic Liquids [emim][PF$_6$] and [bmim]-[PF$_6$]. *Fluid Phase Equilib.* **2002**, *194−197*, 1089−1095.

(9) Domanska, U.; Marciniak, A. Solubility of 1-Alkyl-3-Methylimidazolium Hexafluorophosphate in Hydrocarbons. *J. Chem. Eng. Data* **2003**, *48* (3), 451−456.

(10) Heintz, A.; Lehmann, J. K.; Wertz, C. Thermodynamic Properties of Mixtures Containing Ionic Liquids. 3. Liquid−Liquid Equilibria of Binary Mixtures of 1-Ethyl-3-Methylimidazolium Bis(trifluoromethylsulfonyl)imide with Propan-1-ol, Butan-1-ol, and Pentan-1-ol. *J. Chem. Eng. Data* **2003**, *48* (3), 472−474.

(11) Wu, C.-T.; Marsh, K. N.; Deev, A. V.; Boxall, J. A. Liquid−Liquid Equilibria of Room-Temperature Ionic Liquids and Butan-1-ol. *J. Chem. Eng. Data* **2003**, *48* (3), 486−491.

(12) Selvan, M. S.; McKinley, M. D.; Dubois, R. H.; Atwood, J. L. Liquid−Liquid Equilibria for Toluene + Heptane + 1-Ethyl-3-Methylimidazolium Triiodide and Toluene + Heptane + 1-Butyl-3-Methylimidazolium Triiodide. *J. Chem. Eng. Data* **2000**, *45*, 841−845.

(13) Letcher, T. M.; Deenadayalu, N. Liquid−Liquid Equilibria for Mixtures of 1-Methyl-3-Octyl-Imidazolium Chloride + Benzene + an Alkane at T = 298.2 K and 1 Atm. *J. Chem. Thermodyn.* **2003**, *35*, 67−76.

(14) Letcher, T. M.; Deenadayalu, N.; Soko, B.; Ramjugernath, D.; Naicker, P. K. Ternary Liquid−Liquid Equilibria for Mixtures of 1-Methyl-3-Octylimidazolium Chloride + an Alkanol + an Alkane at 298.2 K and 1 Bar. *J. Chem. Eng. Data* **2003**, *48*, 904−907.

(15) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willanur, H. D.; Broker, G. A.; Rogers, R. D. Characterization and Comparison of Hydrophilic and Hydrophobic Room-Temperature Ionic Liquids Incorporating the Imidazolium Cation. *Green Chem.* **2001**, *3*, 156−164.

(16) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. Organic Solvents. Physical Properties and Methods of Purification, 4th ed., John Wiley & Sons: New York, 1986.

(17) Aminabhavi, T. M.; Aralaguppi, M. Y.; Harogoppad, Sh. B.; Balundgi, R. H. Densities, Viscosities, Refractive Indices, and Speeds of Sound for Methyl Acetoacetate + Aliphatic Alcohols (C1−C8). *J. Chem. Eng. Data* **1993**, *38*, 31−39.

(18) Perry, R. H.; Green, D. W.; Maloney, J. O. *Perry's Chemical Engineers' Handbook*, 7th ed.; McGraw-Hill: New York, 1997.

(19) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1975**, *21*, 116−118.

(20) Sϕrensen, J. M. Doctoral Thesis, Danmarks Tekniske Hϕjskole, Denmark, 1980.

(21) Sϕrensen, J. M.; Arlt, W. *Liquid−Liquid Equilibrium Data Collection*; DECHEMA Chemistry Data Series: Frankfurt, 1980.

(22) Arce, A.; Martínez-Ageitos, J.; Rodríguez, O.; Soto, A. (Liquid + Liquid) Equilibria of (*tert*-Amyl Ethyl Ether + Ethanol + Water) at Several Temperatures. *J. Chem. Thermodyn.* **2001**, *33*, 139−146.

Received for review August 11, 2003. Accepted March 1, 2004. The authors are grateful to the Ministerio de Ciencia y Tecnología of Spain for financial support (Project PPQ2003-01326).

JE0302147