

Ternary Liquid–Liquid Equilibria for Mixtures of 1-Methyl-3-octylimidazolium Chloride + an Alkanol + an Alkane at 298.2 K and 1 bar

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Ternary liquid–liquid equilibria for the mixtures (1-methyl-3-octylimidazolium chloride + an alkanol + an alkane) at 298.2 K are reported. The alkanes used were heptane, dodecane, and hexadecane, and the alkanols were methanol and ethanol. The solubility of the alkanol is higher in the ionic liquid rich phase than in the alkane rich phase. The effectiveness of extracting an alkanol from mixtures containing an alkane using the solvent 1-methyl-3-octylimidazolium chloride is discussed in terms of the ratio of the solubilities in the two phases. The NRTL equation was used to correlate the experimental tie lines. There are no data in the literature for the mixtures discussed in this paper.

Introduction

This work is part of our investigations on ionic liquids¹ as potential solvents for separating liquids using a solvent extraction process. In this work an ionic liquid is used to separate aliphatic compounds and alkanols. The reason for using ionic liquids is that they are environmentally favorable solvents because they do not emit toxic vapors due to their very low vapor pressures.^{2,3}

The data on ternary liquid–liquid equilibria for mixtures containing an ionic liquid are scarce.⁴ In this work the ionic liquid, 1-methyl-3-octylimidazolium chloride (MeOctImCl, see Figure 1) was used. The liquid–liquid equilibrium data for the mixtures (1-methyl-3-octylimidazolium chloride + an alkanol + an alkane) determined at 298.2 K are presented.

The selectivity values for the ternary systems studied in this work were determined in order to investigate the possibility of using MeOctImCl as a solvent in liquid extraction processes. The NRTL equation⁵ was used to correlate the experimental tie line data.

Experimental Section

Chemicals. The alkanols were found to have purities greater than 99% mass, as determined by gas–liquid chromatography, and were stored under 4 Å molecular sieves and found to have less than 0.1% mass water, as determined using Karl–Fischer moisture analysis. The ionic liquid, MeOctImCl, was obtained from Acros and was quoted as having a purity greater than 98 mass %. The sample was subjected to a vacuum of 10⁻⁵ Torr for 30 to 60 min at a temperature of 398 K. The mass loss, as a result of the vacuum treatment, was measured and found to be 0.02 mass fraction. A Karl Fischer titration showed

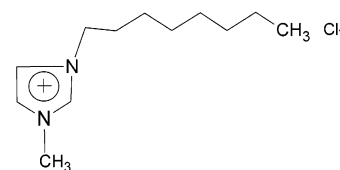


Figure 1. 1-Methyl-3-octylimidazolium chloride (MeOctImCl).

Table 1. Physical Properties of the Pure Components at 298.2 K: Density, ρ , Molar Volumes, V_m , and Molar Mass, M

compd	$\rho(\text{lit.})^{10}$ g·cm ⁻³	$\rho(\text{exp})$ g·cm ⁻³	V_m cm ³ ·mol ⁻¹	M g·mol ⁻¹
MeOctImCl	1.00	1.0104	228.39	230.78
hexadecane	0.7700	0.7703	294.07	226.44
dodecane	0.7487	0.7466	221.22	170.34
heptane	0.6837	0.6823	147.47	100.20
methanol	0.78637	0.78627	40.74	32.04
ethanol	0.78493	0.78493	58.69	46.06

that the water content, after the vacuum treatment, was less than 0.0001 mass fraction. The alkanes were supplied by Acros and had purities greater than 99 mass % and were used without further treatment. The densities, molar volumes, and molar masses of the pure compounds at 298.2 K are reported in Table 1.

Procedure. The binodal curves were determined at 298.2 K and 1 bar pressure using the cloud point method described in detail by Letcher and Siswana.⁶ However, the densities of the one-phase region were determined instead of the refractive index. We found that the density measurements were more reliable than the refractive index. First, a standard calibration curve of composition versus density was determined by measuring the densities of the binary one-phase mixtures: (MeOctImCl + an alkanol) and (an alkanol + an alkane). The densities were measured with a Paar densitometer controlled to within 0.005 K. Tie line compositions were determined from the standard density curves, using a procedure similar to the refractive index

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Table 2. Compositions of Points on the Coexistence Curve at 298.2 K for the Ternary Mixtures [MeOctImCl (1) + an Alkanol (2) + an Alkane (3)]

x_1	x_2	x_1	x_2	x_1	x_2
C ₁₂ H ₂₃ N ₂ ·Cl (1) + CH ₃ OH (2)					
+ C ₇ H ₁₆		+ C ₁₆ H ₃₄			
0.000	0.902	0.000	0.008		
0.007	0.000	0.010	0.000		
0.090	0.850	0.100	0.898		
0.183	0.728	0.139	0.859		
0.235	0.697	0.245	0.750		
0.282	0.641	0.295	0.700		
0.384	0.533	0.411	0.582		
0.463	0.447	0.492	0.501		
0.466	0.439	0.690	0.297		
0.546	0.365	0.712	0.278		
0.551	0.346	0.873	0.111		
0.622	0.274	0.903	0.078		
0.737	0.179	0.981	0.000		
0.935	0.000				
C ₁₂ H ₂₃ N ₂ ·Cl (1) + CH ₃ CH ₂ OH (2)					
+ C ₇ H ₁₆		+ C ₁₂ H ₂₆		+ C ₁₆ H ₃₄	
0.007	0.000	0.009	0.000	0.000	0.956
0.007	0.007	0.008	0.535	0.010	0.000
0.007	0.003	0.027	0.875	0.097	0.876
0.029	0.489	0.077	0.860	0.125	0.846
0.062	0.678	0.098	0.859	0.221	0.758
0.264	0.574	0.140	0.810	0.279	0.709
0.306	0.536	0.270	0.684	0.291	0.693
0.360	0.489	0.286	0.672	0.306	0.679
0.454	0.400	0.315	0.651	0.451	0.538
0.493	0.371	0.430	0.532	0.459	0.532
0.634	0.241	0.481	0.482	0.480	0.513
0.935	0.000	0.500	0.478	0.543	0.449
		0.694	0.294	0.586	0.407
		0.890	0.009	0.599	0.396
		0.923	0.064	0.981	0.000
		0.976	0.000		

method described by Briggs and Comings.⁷ The tie line data were determined using this method because the normal GLC method could not be used due to the extremely low vapor pressure of the ionic liquid. All composition measurements were accurate to within 0.002 mole fraction.

Results

The compositions of the mixtures (mole fractions) on the binodal curve at 298.2 K are given in Table 2. The compositions of the conjugate phases are given in Table 3. The binodal curve and tie line results have been plotted in Figure 2.

Discussion

The solubility of MeOctImCl in an alkane and the solubility of the alkane in MeOctImCl are given in Table 4. The solubility of the alkanes in the alkanols and the solubility of the alkanols in the alkanes are also given in Table 4. The binary mixtures (MeOctImCl + an alkanol) are completely miscible for all the alkanols investigated in this work.

From the results in Table 3 and Figure 2 it can be seen that as the chain length of the alkane increases, there is an increase in the area of the two-phase region which indicates the reduction in the mutual solubility of the components of the mixture.

From the slope of the tie lines (see Figure 2), it can be seen that, in all cases, the alkanols are more soluble in the MeOctImCl rich phase than in the alkane rich phase.

The effectiveness of extracting the alkanol from the alkane by MeOctImCl is given by the selectivity (S),⁸ which

Table 3. Compositions of the Conjugate Solutions and the Selectivities, S , at 298.2 K for the System MeOctImCl (1) + an Alkanol (2) + an Alkane (3)^a

x'_1	x'_2	x''_1	x''_2	S
C ₁₂ H ₂₃ N ₂ ·Cl (1) + CH ₃ OH (2) + C ₇ H ₁₆				
0.183	0.728	0.000	0.020	401
0.463	0.447	0.000	0.001	5000
0.546	0.365	0.001	0.0005	8200
C ₁₂ H ₂₃ N ₂ ·Cl (1) + CH ₃ CH ₂ OH (2) + C ₇ H ₁₆				
0.493	0.371	0.007	0.007	384
0.360	0.489	0.007	0.007	457
0.264	0.574	0.007	0.007	503
C ₁₂ H ₂₃ N ₂ ·Cl (1) + CH ₃ CH ₂ OH (2) + C ₁₂ H ₂₆				
0.923	0.064	0.001	0.006	814
0.430	0.532	0.001	0.007	2000
0.270	0.684	0.001	0.007	2110
0.140	0.810	0.002	0.008	2000
C ₁₂ H ₂₃ N ₂ ·Cl (1) + CH ₃ OH (2) + C ₁₆ H ₃₄				
0.873	0.111	0.001	0.0003	23100
0.690	0.297	0.001	0.0003	76100
0.411	0.582	0.001	0.0003	27700
0.245	0.750	0.001	0.0003	500000
0.139	0.859	0.0004	0.0006	715000
C ₁₂ H ₂₃ N ₂ ·Cl (1) + CH ₃ CH ₂ OH (2) + C ₁₆ H ₃₄				
0.125	0.846	0.001	0.002	14500
0.221	0.758	0.000	0.002	18000
0.306	0.679	0.001	0.001	45200
0.460	0.532	0.001	0.000	33200
0.587	0.407	0.001	0.000	33900

^a The superscript ' indicates the ionic liquid rich phase, and the '' indicates the alkane rich phase.

Table 4. Solubilities of the Binary Mixtures Studied in This Work at 298.2 K

binary mixtures	mole fraction
C ₁₂ H ₂₃ N ₂ ·Cl in C ₇ H ₁₆	0.007
C ₁₂ H ₂₃ N ₂ ·Cl in C ₁₂ H ₂₆	0.009
C ₁₂ H ₂₃ N ₂ ·Cl in C ₁₆ H ₃₄	0.010
C ₇ H ₁₆ in C ₁₂ H ₂₃ N ₂ ·Cl	0.065
C ₁₂ H ₂₆ in C ₁₂ H ₂₃ N ₂ ·Cl	0.024
C ₁₆ H ₃₄ in C ₁₂ H ₂₃ N ₂ ·Cl	0.019
C ₇ H ₁₆ in CH ₃ OH	0.098
C ₁₆ H ₃₄ in CH ₃ OH	0.002
C ₁₆ H ₃₄ in CH ₃ CH ₂ OH	0.044

is the measure of the ability of MeOctImCl to separate an alkanol from an alkane:

$$S = (x'_2/x'_3)/(x''_2/x''_3) \quad (1)$$

The ' refers to the ionic liquid rich phase, the '' refers to the alkane rich phase, and the subscripts 2 and 3 represent the alkanol and the alkane, respectively. This quantity is large for all the systems reported here, which means that extraction of the alkanol by MeOctImCl is possible. Table 2 lists the selectivity (S) values. The order of selectivity is methanol > ethanol for the ternary mixture (MeOctImCl + an alkanol + an alkane). The order of selectivity of MeOctImCl for an alkanol in an alkane mixture is hexadecane > dodecane > octane; that is, the selectivity decreases as the alkane carbon number decreases. The separation could be very useful in the Fischer–Tropsch process where alkanols are produced together with alkanes. The use of ionic liquids in this type of separation is particularly advantageous because it is relatively easy to separate the ionic liquid from the alkanol by distillation because of the low vapor pressure of the ionic liquid.

The nonrandom two liquid equation (NRTL)⁵ was used to correlate the experimental data for the ternary mixtures reported here. The equations and algorithms used in the

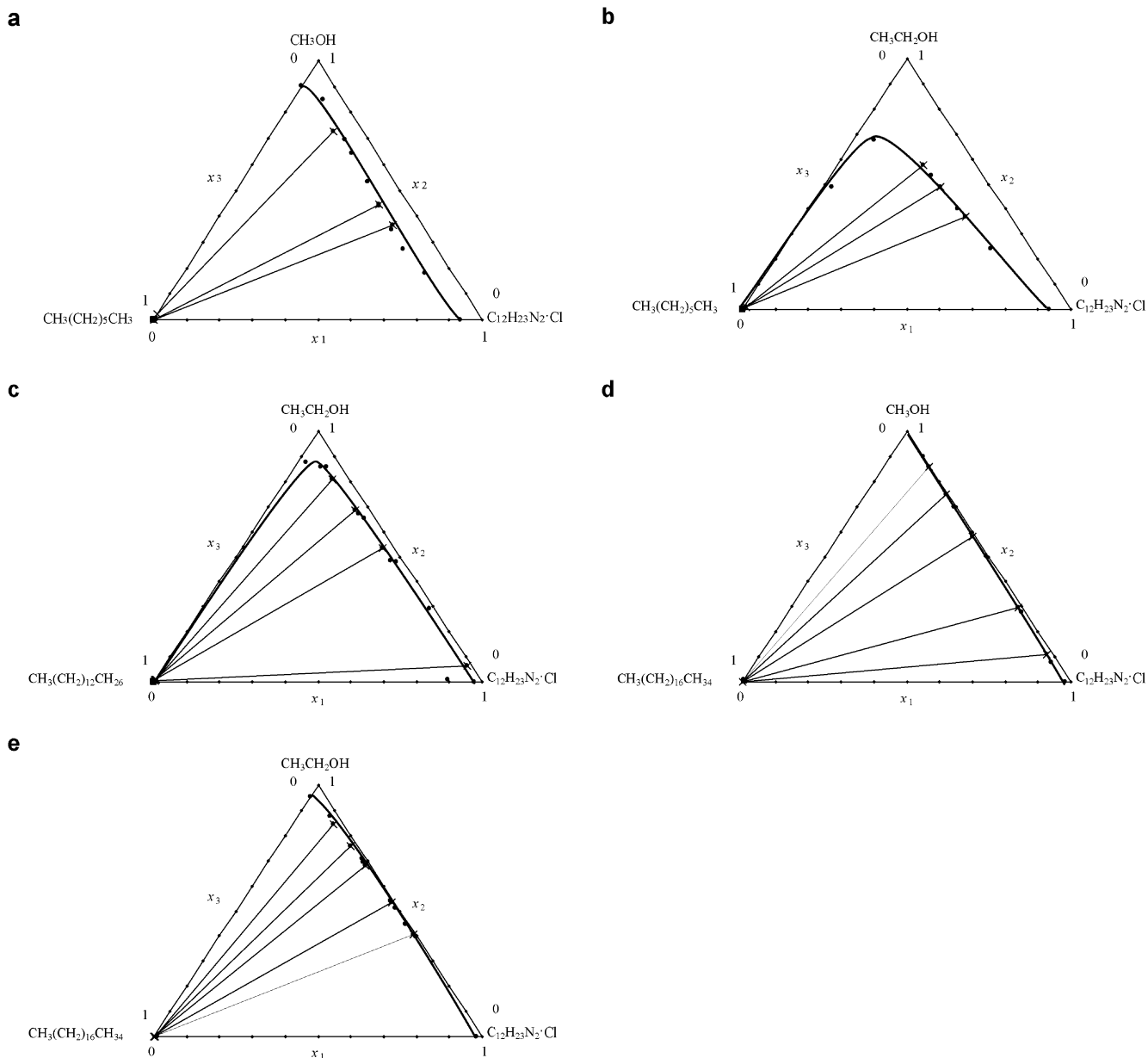


Figure 2. Binodal curves and tie lines for [MeOctImCl (1) + an alkanol (2) + an alkane (3)] at 298.2 K: (a) $x_1\text{C}_{12}\text{H}_{23}\text{N}_2\cdot\text{Cl} + x_2\text{CH}_3\text{OH} + x_3\text{C}_7\text{H}_{16}$; (b) $x_1\text{C}_{12}\text{H}_{23}\text{N}_2\cdot\text{Cl} + x_2\text{CH}_3\text{CH}_2\text{OH} + x_3\text{C}_7\text{H}_{16}$; (c) $x_1\text{C}_{12}\text{H}_{23}\text{N}_2\cdot\text{Cl} + x_2\text{CH}_3\text{CH}_2\text{OH} + x_3\text{C}_{12}\text{H}_{26}$; (d) $x_1\text{C}_{12}\text{H}_{23}\text{N}_2\cdot\text{Cl} + x_2\text{CH}_3\text{OH} + x_3\text{C}_{16}\text{H}_{34}$; (e) $x_1\text{C}_{12}\text{H}_{23}\text{N}_2\cdot\text{Cl} + x_2\text{CH}_3\text{CH}_2\text{OH} + x_3\text{C}_{16}\text{H}_{34}$.

Table 5. Values of the Parameters for the NRTL Equation, Determined from Liquid–Liquid Equilibria for the Ternary Mixtures [MeOctImCl (1) + an Alkanol (2) + an Alkane (3)] at 298.2 K, as Well as the rmsd Values

mixture	α_{ij}	$g_{12} - g_{22}$	$g_{21} - g_{11}$	$g_{13} - g_{33}$	$g_{31} - g_{11}$	$g_{23} - g_{33}$	$g_{32} - g_{22}$	rmsd
$\text{C}_{12}\text{H}_{23}\text{N}_2\cdot\text{Cl} + \text{CH}_3\text{OH} + \text{C}_7\text{H}_{16}$	0.30	-8323.39	-10728.64	5101.57	9591.28	3901.23	5494.82	0.000
$\text{C}_{12}\text{H}_{23}\text{N}_2\cdot\text{Cl} + \text{CH}_3\text{CH}_2\text{OH} + \text{C}_7\text{H}_{16}$	0.30	8661.97	5056.92	3784.19	11181.10	2182.29	11506.72	0.001
$\text{C}_{12}\text{H}_{23}\text{N}_2\cdot\text{Cl} + \text{CH}_3\text{CH}_2\text{OH} + \text{C}_{12}\text{H}_{26}$	0.35	12388.22	7559.62	14575.86	18128.61	4605.80	19627.42	0.003
$\text{C}_{12}\text{H}_{23}\text{N}_2\cdot\text{Cl} + \text{CH}_3\text{OH} + \text{C}_{16}\text{H}_{34}$	0.30	-4848.85	-4620.48	6508.40	25024.64	10861.89	16434.32	0.000
$\text{C}_{12}\text{H}_{23}\text{N}_2\cdot\text{Cl} + \text{CH}_3\text{CH}_2\text{OH} + \text{C}_{16}\text{H}_{34}$	0.35	-3291.77	-17072.42	8983.80	12332.89	8716.45	14556.24	0.004

calculation of the composition of the liquid phases follow the method used by Walas.⁹ The objective function, OF, used to minimize the difference between the experimental and calculated concentrations is defined as

$$\text{OF} = \sum_{k=1}^n \sum_{l=1}^2 \sum_{i=1}^3 (x_{kli} - \bar{x}_{kli})^2 \quad (2)$$

where x_{kli} is the experimental composition of component i in phase l for k th tie line and \bar{x}_{kli} is the calculated composition of component i in phase l for k th tie line. For

the NRTL model, the nonrandomness parameter, α_{ij} , was set at a value of 0.30 or 0.35 (see Table 5). The NRTL equation was optimized for all parameters. The parameters calculated in this way, $g_{ij} - g_{ij}$, $g_{ji} - g_{ji}$, and Δu_{ij} , Δu_{ji} for the NRTL equation are shown in Table 5. The root-mean-square deviation (rmsd) values, defined below, which can be taken as a measure of the precision of the correlation, are also included in Table 5:

$$\text{rmsd} = \left(\sum_i \sum_l \sum_m [x_{ilm}^{\text{exp}} - x_{ilm}^{\text{calc}}]^2 / 6k \right)^{1/2} \quad (3)$$

where x is the mole fraction and the subscripts i , l , and m designate the component, phase, and tie line, respectively, and k designates the number of interaction components. The correlation obtained with the NRTL model is excellent, which shows the reliability of the model to fit tie line data for an ionic liquid.

Literature Cited

- (1) Letcher, T. N.; Deenadayalu, N. Ternary Liquid–liquid Equilibria for mixtures of 1-methyl-3-octyl-imidazolium chloride + benzene + an alkane at 298.2 K and 1 atm. *J. Chem. Thermodyn.* **2003**, *35*, 67–76.
- (2) Freemantle, M. Designer Solvents. *Chem. Eng. News* **1998**, *76*, 32–37.
- (3) SOLVENT INNOVATION, <http://www.solvent-innovation.de>.
- (4) Selvan, M. S.; McKinley, M. D.; Dubois, R. H.; Atwood, J. L. Liquid–liquid Equilibria for the Toluene + Heptane + 1-Ethyl-3-methylimidazolium triiodide and Toluene + Heptane + 1-Butyl-3-methylimidazolium triiodide. *J. Chem. Eng. Data* **2000**, *45*, 841–845.
- (5) Renon, H.; Prausnitz, J. M. Local Composition in Thermodynamics excess function for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.
- (6) Letcher, T. M.; Siswana, P. M. Liquid–liquid equilibria for mixtures of an alkanol + water + a methyl substituted benzene at 25 °C. *Fluid Phase Equilib.* **1992**, *72*, 203–217.
- (7) Briggs, S. W.; Comings, E. W. Effect of temperature on liquid–liquid equilibrium. Benzene-acetone–water and dodecane-1,6-diphenylhexane-furfural systems. *Ind. Eng. Chem.* **1943**, *35*, 411–417.
- (8) Walas, S. W. *Phase Equilibria in Chemical Engineering*, Butterworth Publishers: Boston, MA, 1985.
- (9) Perry, R. H.; Green, D. W.; Maloney, J. O. *Perry's chemical engineers' handbook*, 7th ed.; McGraw-Hill: New York, 1997.
- (10) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; 1986; Vol. ii, pp 190–205.

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