Liquid−Liquid Equilibria for Mixtures of Acetonitrile + a Carboxylic Acid + Heptane at 298.15 K

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Liquid−liquid equilibrium data are presented for mixtures of (acetonitrile + a carboxylic acid + heptane) at 298.15 K. The carboxylic acids (C2−C5) are acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid, and 3-methylbutanoic acid. The relative mutual solubility of all the carboxylic acids is higher in the acetonitrile layer than in the hydrocarbon layer. The influence of 3-methylbutanoic acid, pentanoic acid, 2-methylpropanoic acid, and butanoic acid on the solubility of the hydrocarbons in acetonitrile is greater than that of the acetic and propanoic acids. Three three- parameter equations have been fitted to the binodal curve data. These equations are compared and discussed in terms of statistical consistency. Selectivity values for solvent separation efficiency were derived from the equilibrium data. The NRTL and UNIQUAC models were used to correlate the experimental results and to calculate the phase compositions of the ternary systems. The NRTL equation fitted the experimental data far better than the UNIQUAC equation.

Introduction

A great number of industrial separation processes are concerned with liquid mixtures containing aromatics (benzene, toluene, *p*-xylene, alkylbenzenes, etc.) and saturated hydrocarbons (hexane, heptane, octane, decane, dodecane, etc.). According to Bailes (1977), solvents such as sulfur dioxide, *N*-methylpyrrolidone, *N*-formylmorpholine, dimethyl sulfoxide, and tetrahydrothiophene 1,1-dioxide (sulfolane) have been used extensively in liquid−liquid extraction processes.

Acetonitrile, a relatively inert and inexpensive solvent, with a high density and low viscosity is also an important solvent with liquid−liquid extraction potential capabilities. Liquid−liquid equilibria (LLE) data on a few ternary mixtures containing acetonitrile have been published in the literature: (acetonitrile + benzene + heptane) at 318.15 K by Palmer and Smith (1972); (acetonitrile + ethanol or 1-propanol + hexane or heptane or octane) at 298.15 K by Nagata (1987); and (acetonitrile + benzene or toluene + cyclohexane) at 298.15 K and 318.15 K by Nagata and Ohta (1983).

This work forms part of a program to determine LLE for industrially useful mixtures. LLE data on systems containing acetonitrile + carboxylic acid mixtures are relatively scarce, and in this work the LLE for (acetonitrile + a carboxylic acid + heptane) mixtures have been determined for each of the C2, C3, C4, and C5 carboxylic acids at 298.15 K.

The binodal curve data have been summarized using a modified Hlavatỳ equation (Hlavatỳ, 1972), a β function, and a log γ equation using methods previously described by Letcher et al. (1990). The tie lines were correlated using the NRTL model of Renon and Prausnitz (1968) and the UNIQUAC model of Abrams and Prausnitz (1975).

Experimental Section

Chemicals. The acids were obtained from Acros Chemicals. The compounds were dried using activated type 4 Å molecular sieves and analyzed using the Karl-Fischer technique, showing that the water content was less than 0.01 mass %. Acetonitrile and heptane were purchased from Aldrich Chemical Co. The purity of each of these components was determined by GLC and was always better than 99.8 mol %. The measured physical properties of the reagents used in this work are listed in Table 1 together with literature values.

Procedure. The binodal curves were carried out by the titration method described by Letcher and Siswana (1992). The tie lines were analyzed by the refractive index method of Briggs and Comings (1943), previously used and described by Letcher and Siswana (1992). The estimated precision of the composition of mixtures on the binodal curve was within 5×10^{-3} mole fraction, and that of the tie lines was within 1×10^{-3} mole fraction.

Results

The compositions of mixtures on the binodal curve at 298.15 K are given in Table 2, and tie-line compositions are given in Table 3. These compositions are plotted in Figure 1a−f. Three equations have been fitted to the data following the work of Hlavatỳ (1972). The coefficients A_i relate to a modified Hlavatỳ equation

$$x_2 = A_1 x_A \ln x_A + A_2 x_B \ln x_B + A_3 x_A x_B \qquad (1)$$

the coefficients B_i relate to a β function equation

$$x_2 = B_1 (1 - x_A)^{B_2} {x_A}^{B_3} \qquad (2)$$

and the coefficients C_i relate to the log γ equation

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10.1021/je990112+ CCC: $18.00

Table 1. Physical Properties of the Pure Components at 298.15 K: Molar Volumes, V_{mi}, Refractive Indices, n_D, and Volume and Surface Parameters, R and Q

component	$V_{mi}{}^a$/(cm^3·mol^{-1})	n_D expt	n_D lit^a	R^b	Q^b
acetonitrile	52.87	1.3413	1.3416	1.870	1.724
acetic acid	57.53	1.3697	1.3698	2.202	2.072
propanoic acid	74.97	1.3846	1.3843	2.877	2.612
butanoic acid	92.43	1.3955	1.3958	3.551	3.152
2-methylpropanoic acid	93.44	1.3913	1.3917	3.550	3.148
pentanoic acid	109.29	1.4064	1.4060	4.226	3.692
3-methylbutanoic acid	110.54	1.4019	1.4022	4.225	3.688
heptane	147.47	1.3851	1.3851	5.174	4.396

[a] Riddick et al. (1986). [b] Gmehling et al. (1993).

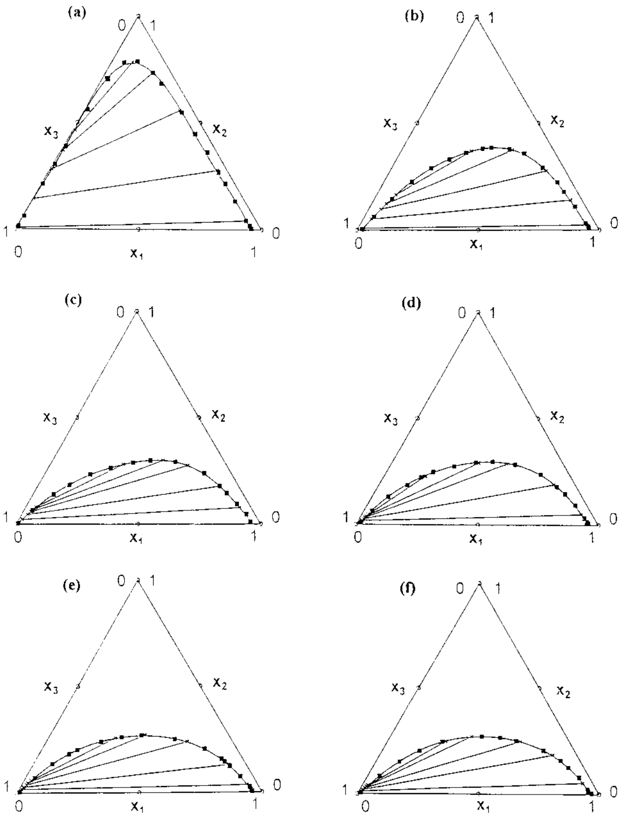

Figure 1. Liquid−liquid equilibrium data for the following systems at 298.15 K: (a) acetonitrile (1) + acetic acid (2) + heptane (3); (b) acetonitrile (1) + propanoic acid (2) + heptane (3); (c) acetonitrile (1) + butanoic acid (2) + heptane (3); (d) acetonitrile (1) + 2- methylpropanoic acid (2) + heptane (3); (e) acetonitrile (1) + pentanoic acid (2) + heptane (3); (f) acetonitrile (1) + 3-methylbutanoic acid (2) + heptane (3). [Key: (■) experimental points; (×) experimental tie lines.]

$$x_2 = C_1(-\ln x_A)^{C_2} x_A{}^{C_3} \tag{3}$$

where

$$x_A = (x_1 + 0.5x_2 - x_1{}^0)/(x_{11}{}^0 - x_1{}^0) \tag{4}$$

$$x_B = (x_{11}{}^0 - x_1 - 0.5x_2)/(x_{11}{}^0 - x_1{}^0) \tag{5}$$

Table 2. Composition of Points on the Binodal Curve at 298.15 K for the Systems Acetonitrile (1) + a Carboxylic Acid (2) + Heptane (3), Equilibrium Mole Fractions, x_1 and x_2

x_1	x_2	x_1	x_2	x_1	x_2
Acetic Acid					
0.956	0.004	0.504	0.448	0.180	0.706
0.942	0.017	0.400	0.547	0.011	0.560
0.915	0.041	0.252	0.682	0.007	0.388
0.824	0.133	0.191	0.732	0.006	0.305
0.743	0.216	0.103	0.786	0.005	0.211
0.689	0.270	0.051	0.780	0.004	0.060
0.598	0.362	0.023	0.702	0.003	0.014
Propanoic Acid					
0.952	0.010	0.621	0.290	0.216	0.330
0.943	0.016	0.511	0.353	0.161	0.288
0.928	0.031	0.441	0.377	0.113	0.225
0.844	0.110	0.362	0.385	0.070	0.145
0.768	0.178	0.329	0.380	0.038	0.062
0.715	0.222	0.270	0.361	0.019	0.004
Butanoic Acid					
0.951	0.011	0.649	0.238	0.186	0.234
0.917	0.046	0.506	0.292	0.124	0.184
0.854	0.095	0.401	0.299	0.082	0.140
0.787	0.145	0.335	0.289	0.034	0.065
0.742	0.179	0.255	0.264	0.006	0.004
2-Methylpropanoic Acid					
0.953	0.008	0.642	0.237	0.152	0.223
0.945	0.014	0.511	0.284	0.114	0.186
0.925	0.032	0.411	0.298	0.064	0.131
0.858	0.093	0.345	0.293	0.031	0.064
0.788	0.147	0.264	0.275	0.013	0.009
0.737	0.179	0.190	0.248		
Pentanoic Acid					
0.956	0.004	0.755	0.156	0.145	0.201
0.946	0.012	0.663	0.205	0.120	0.181
0.935	0.025	0.519	0.250	0.075	0.135
0.874	0.072	0.376	0.269	0.036	0.070
0.806	0.122	0.298	0.261	0.007	0.005
0.774	0.143	0.223	0.239		
3-Methylbutanoic Acid					
0.966	0.004	0.759	0.158	0.224	0.244
0.947	0.012	0.665	0.205	0.153	0.202
0.939	0.024	0.529	0.250	0.095	0.151
0.875	0.079	0.455	0.265	0.047	0.084
0.807	0.126	0.377	0.270	0.009	0.006

and x_1 refers to the mole fraction composition of the acetonitrile, x_2 refers to the mole fraction of a carboxylic acid, and $x_{11}{}^0$ and $x_1{}^0$ are the values of x_1 on the binodal curve which cuts the $x_2 = 0$ axis and have been used to summarize the binodal curve data. These three equations have been discussed by Letcher and Siswana (1992). The coefficients A_i, B_i, and C_i are given in Table 4, together with the standard deviation σ, which is defined as

$$\sigma = [\sum [x_2(\text{calc}) - x_2(\text{expt})]^2/(n-3)]^{1/2} \tag{6}$$

where n is the number of data points and 3 is the number of coefficients (Sen and Srivastava, 1990).

The β function equation gave the best overall fit as compared to the Hlavatў equation and log γ function.

Discussion

The binodal curves in Figure 1a−f show that the solubility of heptane in acetonitrile + a carboxylic acid is very much dependent on the type of acid. In the ternary systems, heptane is most soluble in the systems containing butanoic acid, 2-methylpropanoic acid, pentanoic acid, or 3-methylbutanoic acid. For a particular carboxylic acid, heptane is more soluble in acetonitrile for mixtures containing propionic acid than for mixtures containing acetic acid.

Figure 1 shows that the area of the two-phase heterogeneous region for the carboxylic acid mixtures decreases in the following order: 3-methylbutanoic acid ~ pentanoic acid < 2-methylpropanoic acid < butanoic acid < propanoic acid < acetic acid. This implies that the mutual solubility

Table 3. Composition of the Conjugate Solutions, x'_1, x'_2 and x''_1, x''_2, at 298.15 K

hydrocarbon-rich		acetonitrile-rich	
x'_1	x'_2	x''_1	x''_2
Acetonitrile (1) + Acetic Acid (2) + Heptane (3)			
0.002	0.006	0.917	0.042
0.004	0.142	0.681	0.279
0.006	0.281	0.388	0.557
0.007	0.370	0.192	0.732
0.009	0.463	0.085	0.782
Acetonitrile (1) + Propanoic Acid (2) + Heptane (3)			
0.021	0.001	0.936	0.024
0.033	0.052	0.811	0.140
0.050	0.098	0.643	0.275
0.060	0.123	0.455	0.373
0.079	0.165	0.289	0.370
Acetonitrile (1) + Butanoic Acid (2) + Heptane (3)			
0.014	0.022	0.875	0.078
0.025	0.045	0.742	0.179
0.030	0.059	0.566	0.275
0.038	0.073	0.454	0.299
0.040	0.081	0.300	0.281
Acetonitrile (1) + 2-Methylpropanoic Acid (2) + Heptane (3)			
0.015	0.018	0.905	0.050
0.018	0.027	0.721	0.189
0.020	0.032	0.477	0.288
0.021	0.038	0.358	0.292
0.026	0.046	0.169	0.227
Acetonitrile (1) + Pentanoic Acid (2) + Heptane (3)			
0.01	0.017	0.920	0.035
0.012	0.027	0.799	0.130
0.019	0.038	0.578	0.238
0.020	0.047	0.390	0.270
0.028	0.059	0.274	0.258
Acetonitrile (1) + Methylbutanoic Acid (2) + Heptane (3)			
0.010	0.012	0.905	0.053
0.012	0.019	0.715	0.184
0.017	0.028	0.548	0.247
0.020	0.034	0.336	0.270
0.021	0.040	0.240	0.247

of the components is increased as the carbon chain length of the acid is increased and also that heptane is most soluble in the acetonitrile−3-methylbutanoic acid or acetonitrile−pentanoic acid mixture and least soluble in the acetonitrile−acetic acid mixture. The relative solubility of an acid in acetonitrile or the alkane is evident from the tie lines. The slopes of the tie lines obtained in this work show that all the acids are more soluble in the acetonitrile than the alkane (hydrocarbon) mixture. For the C5 acids, the gradient of the tie lines for 3-methylbutanoic acid is greater than those for pentanoic acid. This could be attributable to the greater solubilizing effect of the two methyl groups on the terminal carbon of 3-methylbutanoic acid as opposed to its straight chain isomer. A similar effect is noted for 2-methylpropanoic acid as compared to butanoic acid.

The effectiveness of extraction of a carboxylic acid (2) by acetonitrile is given by its selectivity (ω), which is a measure of the ability of acetonitrile to separate the carboxylic acid (2) from heptane (Letcher et al., 1996):

$$\omega = \text{(distribution coeff of carboxylic acids)}/\text{(distribution coeff of heptane)}$$
$$= [\text{(mole fraction of carboxylic acid (2) in acetonitrile-rich phase)}/\text{(mole fraction of carboxylic acid (2) in heptane-rich phase)}]/[\text{(mole fraction of heptane (3) in acetonitrile-rich phase)}/\text{(mole fraction of heptane (3) in heptane-rich phase)}]$$

Table 4. Coefficients A_i, B_i, and C_i in Equations 1−3 at 298.15 K

Hlavatý	β	$\log \gamma$
Acetonitrile (1) + Acetic Acid (2) + Heptane (3)		
$A_1 = 0.254$	$B_1 = 4.235$	$C_1 = 3.831$
$A_2 = 0.686$	$B_2 = 1.271$	$C_2 = 1.229$
$A_3 = 4.309$	$B_3 = 1.215$	$C_3 = 1.682$
$\sigma = 0.022$	$\sigma = 0.020$	$\sigma = 0.022$
Acetonitrile (1) + Propanoic Acid (2) + Heptane (3)		
$A_1 = 0.297$	$B_1 = 1.633$	$C_1 = 1.523$
$A_2 = -0.269$	$B_2 = 0.925$	$C_2 = 0.896$
$A_3 = 1.552$	$B_3 = 1.182$	$C_3 = 1.531$
$\sigma = 0.010$	$\sigma = 0.009$	$\sigma = 0.010$
Acetonitrile (1) + Butanoic Acid (2) + Heptane (3)		
$A_1 = -0.0018$	$B_1 = 1.001$	$C_1 = 3.831$
$A_2 = -0.473$	$B_2 = 0.766$	$C_2 = 1.229$
$A_3 = 0.942$	$B_3 = 1.001$	$C_3 = 1.682$
$\sigma = 0.006$	$\sigma = 0.007$	$\sigma = 0.008$
Acetonitrile (1) + 2-Methylpropanoic Acid (2) + Heptane (3)		
$A_1 = -0.140$	$B_1 = 0.945$	$C_1 = 0.891$
$A_2 = -0.456$	$B_2 = 0.759$	$C_2 = 0.736$
$A_3 = 0.355$	$B_3 = 0.915$	$C_3 = 1.200$
$\sigma = 0.004$	$\sigma = 0.005$	$\sigma = 0.007$
Acetonitrile (1) + Pentanoic Acid (2) + Heptane (3)		
$A_1 = -0.102$	$B_1 = 0.883$	$C_1 = 0.830$
$A_2 = -0.341$	$B_2 = 0.792$	$C_2 = 0.768$
$A_3 = 0.460$	$B_3 = 0.924$	$C_3 = 1.221$
$\sigma = 0.004$	$\sigma = 0.004$	$\sigma = 0.003$
Acetonitrile (1) + 3-Methylbutanoic Acid (2) + Heptane (3)		
$A_1 = -0.023$	$B_1 = 0.966$	$C_1 = 0.904$
$A_2 = -0.261$	$B_2 = 0.847$	$C_2 = 0.821$
$A_3 = 0.692$	$B_3 = 0.982$	$C_3 = 1.297$
$\sigma = 0.005$	$\sigma = 0.005$	$\sigma = 0.004$

Representative values of selectivity for the middle of the area of the measured tie lines are 26, 29, 27, 36, 32, and 41 for acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid, and 3-methylbutanoic acid, respectively. From the selectivity data, it can be concluded that the separation of all the carboxylic acids from heptane by extraction is feasible. It can also be concluded that acetonitrile is an especially good component for the separation of mixtures of heptane and 2-methylpropanoic acid or heptane and 3-methylbutanoic acid.

Tie-Line Correlation. Thermodynamic models such as the nonrandom two liquid equation NRTL (Renon and Prausnitz, 1968) and the universal quasichemical equation UNIQUAC (Abrams and Prausnitz, 1975) are used to correlate the experimental data for the ternary systems discussed here. The equations and algorithms used in the calculation of the composition of the liquid phases follow the method used by Walas (1985). The objective function used to minimize the difference between the experimental and calculated concentrations is defined as

$$F(P) = \sum_{i=1}^{n} [(x'_{1i})^{\text{expt}} - (x'_{1i}(P,T))^{\text{calc}}]^2 + [(x'_{2i})^{\text{expt}} - (x'_{2i}(P,T))^{\text{calc}}]^2 + [(x''_{1i})^{\text{expt}} - (x''_{1i}(P,T))^{\text{calc}}]^2 + [(x''_{2i})^{\text{expt}} - (x''_{2i}(P,T))^{\text{calc}}]^2 \quad (7)$$

where P is the set of parameters vector, n is the number of experimental points, (x'_{1i}), $(x'_{2i})^{\text{expt}}$, and $(x'_{1i})^{\text{calc}}(P,T))^{\text{calc}}$, $(x'_{2i})(P,T))^{\text{calc}}$ are the experimental and calculated mole fractions of one phase, and $(x''_{1i})^{\text{expt}}$, $(x''_{2i})^{\text{expt}}$, and $(x''_{1i}(P,T))^{\text{calc}}$, $(x''_{2i})(P,T))^{\text{calc}}$ are the experimental and calculated mole fractions of the second phase. The pure component structural parameters R (volume parameter) and Q (surface parameter) in the UNIQUAC equation were obtained

Table 5. Values of the Parameters for the NRTL and UNIQUAC Equations, Determined from Ternary Liquid−Liquid Equilibria for the Systems Acetonitrile (1) + a Carboxylic Acid (2) + Heptane (3) as Well as the Calculated Root Mean Square Deviation, rms[b]

component	parameters ($J \cdot mol^{-1}$)			
	NRTL[a]		UNIQUAC	
i−j	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ji}
Acetonitrile (1) + Acetic Acid (2) + Heptane (3)				
	(0.003)		(0.227)	
1−2 2−1	−2360.27	6107.47	0.20	0.23
1−3 3−1	3606.27	15248.29	−0.10	0.03
2−3 3−2	7038.95	−707.69	−8.59	8.53
Acetonitrile (1) + Propanoic Acid (2) + Heptane (3)				
	(0.006)		(0.021)	
1−2 2−1	4693.46	11522.21	−338.94	40853.60
1−3 3−1	6928.49	6076.73	68.66	10939.72
2−3 3−2	916.90	9840.28	619.13	2510.25
Acetonitrile (1) + Butanoic Acid (2) + Heptane (3)				
	(0.019)		(0.242)	
1−2 2−1	66013.37	14504.09	−21.81	−97.54
1−3 3−1	4724.83	6077.16	98.28	78.39
2−3 3−2	4227.85	3160.78	−100.16	18.73
Acetonitrile (1) + 2−Methylpropanoic Acid (2) + Heptane (3)				
	(0.013)		(0.051)	
1−2 2−1	−4705.61	20825.59	−2859.04	−1391.75
1−3 3−1	6819.80	4903.75	1541.87	4593.31
2−3 3−2	−2445.64	8426.63	−309.47	−1549.41
Acetonitrile (1) + Pentanoic Acid (2) + Heptane (3)				
	(0.003)		(0.018)	
1−2 2−1	−43.94	8800.71	1628.90	21818.88
1−3 3−1	6537.71	7980.18	1864.77	40216.15
2−3 3−2	−2709.08	11811.35	−2317.15	12027.50
Acetonitrile (1) + 3-Methylbutanoic Acid (2) + Heptane (3)				
	(0.022)		(0.233)	
1−2 2−1	50216.71	24207.70	2.79	49.45
1−3 3−1	4604.56	5987.53	99.65	70.01
2−3 3−2	4781.79	4074.60	−224.95	−10.01

[a] Calculated with $a_{ij} = 0.2$. [b] The rms deviations are given in parentheses.

from the tables of modified UNIFAC, published by Gmehling et al. (1993) (see Table 1).

For the NRTL model the third randomness parameter α_{ij} was set at a value of 0.2. The parameters calculated in this way, $g_{ji} - g_{jj}$, $g_{ji} - g_{ii}$, and Δu_{ij}, Δu_{ji}, for NRTL and UNIQUAC, respectively, are shown in Table 5. The model correlation parameters are included in Table 5, together with the root mean square values. The root mean square value defined below can be taken as a measure of the precision of the correlations:

$$\mathrm{rms} = \left(\sum_i \sum_l \sum_m [x_{ilm}^{\mathrm{expt}} - x_{ilm}^{\mathrm{calc}}]^2/6k\right)^{1/2} \tag{8}$$

where x is the mole fraction and the subscripts i, l, and m designate the component, phase, and tie line, respectively. As can be observed from Table 5, the correlation obtained with the NRTL model is significantly better than that obtained with the UNIQUAC model: the average root mean square deviation phase composition error was 0.011 for NRTL as compared to 0.132 for UNIQUAC.

Conclusion

Liquid−liquid equilibrium data for the six ternary mixtures [acetonitrile (1) + acetic acid or propanoic acid or butanoic acid or 2-methylpropanoic acid or pentanoic acid or 3-methylbutanoic acid (2) + heptane (3)] were determined at 298.15 K.

The separations of a carboxylic acid from heptane by extraction with acetonitrile are feasible as can be concluded from the distribution and selectivity data. The four carboxylic acids butanoic acid, 2-methylpropanoic acid, pentanoic acid, and 3-methylbutanoic acid are better solvents for the acetonitrile + heptane mixtures than are the other acids at 298.15 K. Three equations have been fitted to the binodal curve data.

Equations relating to the NRTL and UNIQUAC models have been fitted to the experimental tie lines. The better results have been obtained using the NRTL model.

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Received for review April 26, 1999. Accepted June 30, 1999. The authors wish to thank FRD (South Africa) for financial support.

JE990112+