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Ternary Liquid−Liquid Equilibria of Acetonitrile and Water with Heptanoic Acid and Nonanol at 323.15 K and 1 atm

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Liquid−liquid equilibrium data were measured and correlated for the ternary systems acetonitrile + water + heptanoic acid and acetonitrile + water + nonanol at 323.15 K and 1 atm. The liquid−liquid equilibrium data were measured using the direct analytical method in a double-walled glass cell. The binodal curve was correlated using a modified Hlavatý equation, a β function, and a log γ equation. The experimental tie lines were correlated using the NRTL and UNIQUAC activity coefficient models. Fitting of both activity coefficient models was undertaken by nonlinear least-squares regression of the data. The tie-line data were used to derive the selectivity values for solvent separation efficiency.

Introduction

Mixtures of acetonitrile and water are produced by several processes in the chemical industry. Acetonitrile is primarily used as an extractive solvent for unsaturated hydrocarbons and as a general purpose solvent for many compounds due to its selective miscibility. However, it is not possible to separate acetonitrile from water by common distillation, as these components form a minimum boiling point azeotrope.[1] This study therefore involved the selection of a suitable solvent (preferably a heavy carboxylic acid or alcohol) to separate acetonitrile from water. Hence, ternary liquid−liquid equilibrium measurements of acetonitrile and water with heptanoic acid and nonanol were undertaken at 323.15 K and 1 atm. The data presented have never been reported previously in the open literature.

Experimental

Chemicals. All chemicals used in this research were purchased from Merck, except for water which was distilled in our laboratory. The chemicals were used without further purification as gas chromatographic (GC) analysis revealed no significant impurities. Table 1 shows the mass percentage of the chemicals as provided by the supplier, as well as the peak area percentages obtained from GC analysis and the measured refractive indices. The *R*, *Q*, and *Q′* UNIQUAC parameters are listed in Table 2.

Equipment. The liquid−liquid equilibrium measurements were undertaken using a direct analytical double-walled glass cell with flat bladed impellers for agitation of the contents. The cell design and full description is given by Ndlovu and others,[2−4] and a schematic of the cell is shown in Figure 1.

A Pt-100 temperature sensor, which was placed in a thermowell in the cell, was used to measure the temperature of the cell with a precision of 0.02 °C. Water was circulated through the cell wall and lid from a constant temperature bath. The experimental procedure was performed using the method described by Alders.[5] For each measurement, the contents of the cell were agitated for approximately one hour at low speed to prevent emulsification.

The samples were analyzed by gas chromatography using a Chrompack 9000 GC which was fitted with a thermal conductivity detector. A 2 m × 1/8″ stainless steel tenax TA 80/100 packed column was used for the analysis. Helium was used as the carrier gas. The estimated precision of the mole fraction composition was within $1 \cdot 10^{-4}$.

Table 1. Chemical Purity

chemical	gc analysis (peak area %)	minimum purity[a] (mass %)	measured refractive indices	refractive indices[16]
acetonitrile	99.90	99.9	1.3441	1.3442
heptanoic acid	99.32	99	1.4175	1.4170
1-nonanol	99.14	98	1.4322	1.4340
water[b]	99.80	-	1.3330	1.3328

[a] Stated by supplier. [b] Electrical conductivity of 0.0015 Siemens·m^{-1}.

Table 2. Structural Parameters for the UNIQUAC Model

	acetonitrile	heptanoic acid	1-nonanol	water
R^a	1.87	6.71	6.62	0.92
Q^a	1.72	6.31	5.83	1.40
$(Q')^a$	1.72	6.31	5.83	1.00

[a] Ref 13.

Data Correlation

Binodal Curve. The liquid−liquid binodal curve was correlated using three equations presented in the work of Hlavatý:[6]

1) The Hlavatý equation with coefficients A_i

$$x_3 = A_1 x_A \ln x_A + A_2 x_B \ln x_B + A_3 x_A x_B \tag{1}$$

2) The β function equation[7] with coefficients B_i

$$x_3 = B_1 (1 - x_A)^{B_2} x_A^{B_3} \tag{2}$$

3) The log γ equation[8] with coefficients C_i

$$x_3 = C_1 (-\ln x_A)^{C_2} x_A^{C_3} \tag{3}$$

with

$$x_A = (x_2 + 0.5x_3 - x_2^0)/(x_{22}^0 - x_2^0) \tag{4}$$

$$x_B = (x_{22}^0 - x_2 - 0.5x_3)/(x_{22}^0 - x_2^0) \tag{5}$$

In all the above equations x_2 refers to the mole fraction composition of water; x_3 refers to the mole fraction composition

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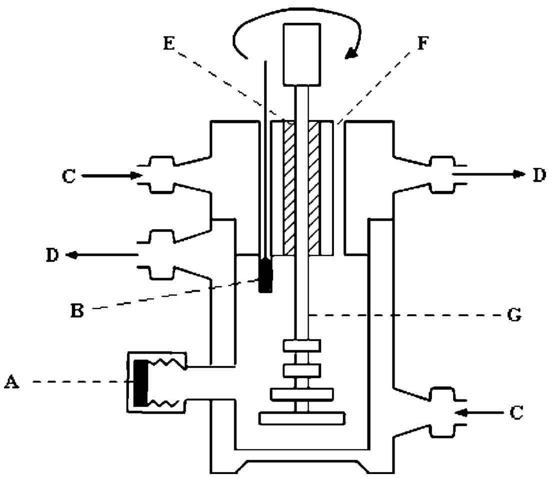

Figure 1. Schematic diagram of the LLE cell.[2] **A**, sample point for denser liquid phase; **B**, Pt-100 temperature sensor in a thermo-well; **C**, ethylene glycol solution into the LLE cell jacket; **D**, ethylene glycol solution away from the LLE cell; **E**, Teflon bushing; **F**, sample point for lighter liquid phase; **G**, stirrer driven by DC motor.

of acetonitrile; and x_2^0 and x_{22}^0 are the values of x_2 on the binodal curve which cuts the $x_3 = 0$ axis.

The β function equation was proposed by Letcher et al.[7] and the log γ equation by Letcher et al.[8] For both these equations, the choice of independent variables avoids the problem of the variables being highly intercorrelated. Equations 1 to 3 were fitted to the binodal curves with the standard deviations σ defined as

$$\sigma = \left\{ \sum_{k=1}^{n} [x_3(\text{calc}) - x_3(\text{exp})]_k^2/(n-3) \right\}^{1/2} \tag{6}$$

where n is the number of data points and 3 is the number of estimated coefficients.[9]

Tie-Line Correlation. The thermodynamic criterion for liquid−liquid phase equilibrium (from equality of the fugacities) is

$$(x_i\gamma_i)^{\text{I}} = (x_i\gamma_i)^{\text{II}} \tag{7}$$

where x is the liquid phase mole fraction; γ is the liquid phase activity coefficient; and I and II denote the respective equilibrium phases.

The tie-lines of the measured liquid−liquid equilibrium data were correlated using the NRTL[10] and UNIQUAC[11] activity coefficient models. The algorithm used for the calculation of the compositions in both phases was based on the method suggested by Walas.[12] The minimization of a nonlinear least-squares objective function was chosen over the maximum likelihood function. The former is more attractive and is suggested by Novak et al.[13] with the following objective function

$$S = \sum_{i=1}^{n} \{[\Delta x_{1,i}^{\text{I}}]^2 + [\Delta x_{2,i}^{\text{I}}]^2 + [\Delta x_{1,i}^{\text{II}}]^2 + [\Delta x_{2,i}^{\text{II}}]^2\} \tag{8}$$

$$\Delta x_{1,i}^{\text{I}} = x_{1,i(\text{exp})}^{\text{I}} - x_{1,i(\text{calc})}^{\text{I}}$$
$$\Delta x_{2,i}^{\text{I}} = x_{2,i(\text{exp})}^{\text{I}} - x_{2,i(\text{calc})}^{\text{I}}, \text{ etc.}$$

where n is the number of experimental points; x is the mole fraction composition; subscripts 1 and 2 denote components 1 and 2, respectively; (exp) and (calc) denote the experimental and calculated mole fraction compositions, respectively; and I and II denote the two phases in equilibrium.

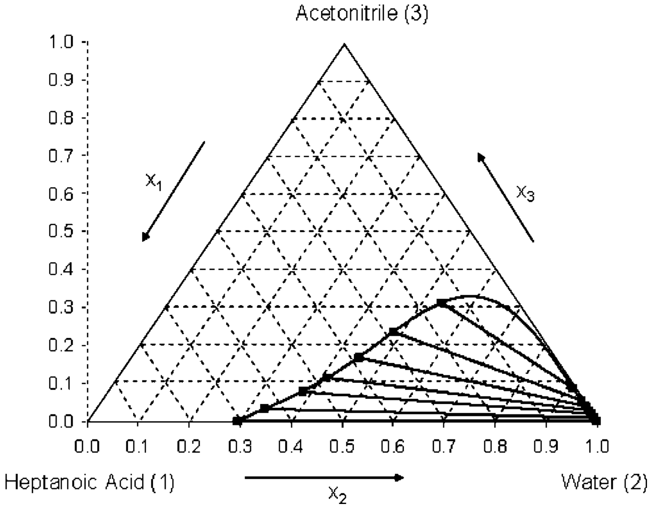

Figure 2. Liquid−liquid equilibrium for the system heptanoic acid (1) + water (2) + acetonitrile (3) at 323.15 K and 1 atm: ●, experimental.

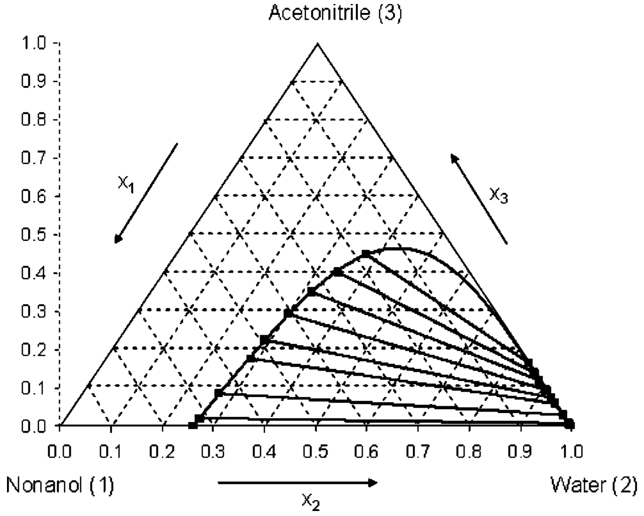

Figure 3. Liquid−liquid equilibrium for the system nonanol (1) + water (2) + acetonitrile (3) at 323.15 K and 1 atm: ●, experimental.

The nonrandomness parameter, α_{ij}, in the NRTL model, was set to the same value for all three binary pairs and fixed at either 0.20, 0.25, 0.30, 0.35, or 0.40 (as suggested in Walas[12]) in the optimization algorithm. Hence, the number of regression parameters was reduced from nine to six. The root-mean-square deviation (rmsd) gave an indication of the "degree of fit" of the correlation

$$\text{rmsd} = \left\{ \frac{\sum_a \sum_b \sum_c \{x_{abc}(\text{exp}) - x_{abc}(\text{calc})\}^2}{6k} \right\}^{1/2} \tag{9}$$

where x is the mole fraction; k is the number of experimental points; and the subscripts a, b, and c denote the component, phase, and tie-line, respectively.

Results

The experimental liquid−liquid equilibrium data for the acetonitrile + heptanoic acid + water and acetonitrile + nonanol + water systems are presented graphically in Figures 2 and 3 and tabulated in Tables 3 and 4, respectively. The coefficients from the binodal curve correlations and the standard deviations are provided in Table 5. The correlated NRTL and UNIQUAC model parameters are presented in Table 6.

Table 3. Tie-Line Compositions for the System Heptanoic Acid (1) + Water (2) + Acetonitrile (3) at 323.15 K and 1 atm

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.7047	0.2953	0.0000	0.0016	0.9984	0.0000
0.6366	0.3309	0.0325	0.0017	0.9891	0.0092
0.5386	0.3839	0.0775	0.0019	0.9787	0.0194
0.4739	0.4109	0.1152	0.0021	0.9693	0.0286
0.3839	0.4486	0.1675	0.0024	0.9579	0.0397
0.2823	0.4826	0.2351	0.0036	0.9407	0.0557
0.1489	0.5385	0.3126	0.0040	0.9086	0.0874

Table 4. Tie-Line Compositions for the System Nonanol (1) + Water (2) + Acetonitrile (3) at 323.15 K and 1 atm

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.7396	0.2604	0.0000	0.0035	0.9965	0.0000
0.7163	0.2630	0.0207	0.0023	0.9901	0.0076
0.6460	0.2687	0.0853	0.0026	0.9683	0.0291
0.5391	0.2849	0.1760	0.0028	0.9381	0.0591
0.4872	0.2873	0.2255	0.0037	0.9223	0.0740
0.4091	0.2987	0.2922	0.0027	0.9026	0.0947
0.3329	0.3177	0.3494	0.0035	0.8768	0.1197
0.2557	0.3426	0.4017	0.0034	0.8568	0.1398
0.1782	0.3726	0.4492	0.0020	0.8325	0.1655

Table 5. Coefficients and Standard Deviations for the Binodal Curve Data at 323.15 K and 1 atm

Hlavatý	β	log γ
Heptanoic Acid (1) + Water (2) + Acetonitrile (3)		
$A_1 = 0.7212$	$B_1 = 2.3492$	$C_1 = 2.2095$
$A_2 = -0.1128$	$B_2 = 1.1435$	$C_2 = 1.1244$
$A_3 = 1.9061$	$B_3 = 1.9348$	$C_3 = 2.3945$
$\sigma = 0.0175$	$\sigma = 0.0085$	$\sigma = 0.0091$
Nonanol (1) + Water (2) + Acetonitrile (3)		
$A_1 = 0.4875$	$B_1 = 2.3783$	$C_1 = 2.1411$
$A_2 = 0.2100$	$B_2 = 1.1394$	$C_2 = 1.1016$
$A_3 = 2.7271$	$B_3 = 1.2723$	$C_3 = 1.6885$
$\sigma = 0.0074$	$\sigma = 0.0055$	$\sigma = 0.0066$

Table 6. NRTL and UNIQUAC Interaction Parameters and Root Mean Square Deviations for: {Solvent (1) + Water (2) + Acetonitrile (3)} at 323.15 K and 1 atm

		NRTL Parameters			UNIQUAC Parameters		
i	j	$g_{ij} - g_{jj}$ J·mol^{-1}	$g_{ji} - g_{ii}$ J·mol^{-1}	rmsd	$u_{ij} - u_{jj}$ J·mol^{-1}	$u_{ji} - u_{ii}$ J·mol^{-1}	rmsd
Heptanoic Acid (1) + Water (2) + Acetonitrile (3)							
1	2	1513.50	10192.80		333.74	2105.37	
1	3	2079.09	−879.28		161.60	5478.01	
2	3	7870.01	−224.34	0.0134	−2135.15	6710.40	0.0030
Nonanol (1) + Water (2) + Acetonitrile (3)							
1	2	2091.19	16481.89		−289.81	3107.44	
1	3	406.47	6615.19		939.41	4283.66	
2	3	2854.99	5442.57	0.0065	−950.73	3667.61	0.0023

It can be seen from the liquid−liquid equilibrium data for both systems that the solvent (heptanoic acid or nonanol) is only partially soluble in water (0.0016 mol fraction for heptanoic acid and 0.0035 mol fraction for nonanol). The shape of the binodal curve for the system heptanoic acid + water + acetonitrile curves sharply toward the water-rich region for small amounts of acetonitrile but decreases in sharpness for larger amounts of acetonitrile. This phenomenon was also observed by Garcia et al.[14] who investigated the effect of using heptanoic acid to separate water from ethanol. The nonanol + water + acetonitrile system displays a smooth binodal curve, typical of a type I system.[15]

The standard deviations shown in Table 5 indicate that the binodal curve for each system was best described by the β function equation. The rmsd values listed in Table 6 indicate that the tie-lines were best described by the UNIQUAC model.

The effectiveness of a solvent can be expressed by the selectivity (ω) of the solvent. The selectivity of the solvent (heptanoic acid or nonanol), which is a measure of the ability of a solvent to separate acetonitrile from water, is given by

$$\omega = \frac{(x_3)^{\mathrm{II}}/(x_3)^{\mathrm{I}}}{(x_2)^{\mathrm{II}}/(x_2)^{\mathrm{I}}} \tag{10}$$

where the subscripts 2 and 3 represents water and acetonitrile, respectively, and I and II represent the water-rich phase and solvent-rich phases, respectively.

Representative values of selectivity for the measured tie-lines in the middle of the triangular plot were 9.5 and 9.7 for heptanoic acid and nonanol, respectively. For effective separation, ω must significantly exceed a value of one. It can thus be concluded that the separation of water from acetonitrile by extraction using either heptanoic acid or nonanol is feasible.

Conclusion

This investigation involved the selection of a suitable solvent (preferably a heavy carboxylic acid or alcohol) to separate acetonitrile from water. New liquid−liquid equilibrium data were measured, and the data were correlated for the ternary systems, heptanoic acid + water + acetonitrile and nonanol + water + acetonitrile at 323.15 K and 1 atm. It was found that the separation of acetonitrile from water with either heptanoic acid or nonanol is feasible. The binodal curves were correlated using three equations: the Hlavatý equation, a β function equation, and a log γ equation. For both systems, the β function equation was found to provide the best correlation. The tie-line data were regressed using the NRTL and UNIQUAC liquid phase activity coefficient models. From this analysis, it was found that the UNIQUAC model described both ternary systems very well.

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