

Liquid–Liquid Equilibria for Mixtures of Water + an Alkanol + a Nitrile Compound at $T = 298.15$ K

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Liquid–liquid equilibrium results for mixtures of water + an alkanol + a nitrile compound at $T = 298.15$ K are reported, where an alkanol is methanol, ethanol, or 1-propanol and the nitrile compound is 1,4-dicyanobutane, butanenitrile, or benzonitrile. The NRTL and UNIQUAC models were correlated to the data.

Introduction

Continuing our investigation into the thermodynamic properties of mixtures containing nitrile compounds,^{1,2} the liquid–liquid equilibrium results for the mixtures (water + an alkanol + a nitrile compound) at $T = 298.15$ K are reported, where an alkanol is methanol, ethanol, or 1-propanol and the nitrile compound is 1,4-dicyanobutane, butanenitrile, or benzonitrile. The suitability of these nitrile compounds to separate water–alkanol mixtures was investigated. A literature search for liquid–liquid equilibrium data for the mixtures investigated here showed that only data for the mixtures (water + methanol or ethanol or propanol + benzonitrile) at $T = 298.15$ K have been reported.^{3,4}

The binodal curve data have been summarized by the Hlavatý equation,⁵ a β function, and a log γ function following the work of Letcher et al.⁶

The NRTL model⁷ and the UNIQUAC model⁸ were used to correlate the tie line data.

Experimental Section

The binodal curves were determined at 298.15 K using the cloud point method, described in detail by Letcher and Siswana.⁹ The tie lines were determined using the refractive index method, described in detail by Briggs and Comings.¹⁰ The accuracy of this technique was established in a previous paper¹¹ by comparing results obtained in our laboratory with literature values for a test system and was found to be within 0.005 mole fraction.

The purities of the chemicals were determined by gas chromatography, and the results are recorded in Table 1. Methanol, ethanol, and propanol were treated with calcium hydride and distilled at a reflux ratio of 0.1 using a 1-m-long column filled with glass helices. The alcohols and the nitrile compounds were stored under 4A molecular sieves. The chemicals were analyzed by Karl Fischer moisture titration and contained $<1 \times 10^{-4}$ mole fraction water.

The temperature was controlled to within 0.01 K using a Tronac temperature controller used in conjunction with a calibrated Hewlett-Packard quartz thermometer.

Results

The compositions of points on the binodal curve for the mixtures ($H_2O + C_mH_{2m+1}OH + 1,4-NC(CH_2)_4CN$ or $CH_3-CH_2CH_2CN + C_6H_5CN$) at $T = 298.15$ K are reported in Table 2, where m is the number of carbons atoms in the alkanol. The compositions of conjugate phases for these

Table 1. Details of the Chemicals: Percentage Mole Fraction Purities, UNIQUAC Structural Parameters, and Refractive Indices

compound	purity	UNIQUAC structural parameters			n_D^{25}	
		r	q	q'	exptl	lit. ^a
water	>99.9	0.92	1.40	1.00	1.3326	1.3325
CH ₃ OH	99.7	1.43	0.96	0.96	1.3270	1.3265
CH ₃ CH ₂ OH	99.5	1.97	0.92	0.92	1.3588	1.3594
CH ₃ CH ₂ CH ₂ OH	99.6	2.51	0.89	0.89	1.3847	1.3837
1,4-NC(CH ₂) ₄ CN	>99	3.91	3.91	3.91	1.4365	
CH ₃ CH ₂ CH ₂ CN	99	2.80	2.80	2.80	1.3825	1.3820
C ₆ H ₅ CN	99	3.01	3.01	3.01	1.5252	1.5257

^a Riddick et al.¹³ No literature value could be found for 1,4-dicyanobutane.

mixtures (tie lines) are given in Table 3. The compositions of the plait points or critical points, which were determined following the method of Treybal,¹² are given in Table 4. The ternary phase diagrams showing the binodal curve together with tie lines and plait points are given in Figures 1–9. The ability of the nitrile compound to separate water and alkanol mixtures is indicated by the selectivity, S , defined as

$$S = \{(x_2'/x_1')\}/\{(x_2''/x_1'')\}$$

Value of S are presented in Table 3. The ' refers to the nitrile compound-rich phase and the '' refers to the water-rich phase; the subscripts 1 and 2 indicate water and the alkanol, respectively.

Three equations have been fitted to the binodal curve data following the work of Hlavatý⁵ and Letcher et al.⁶ The coefficients A_i relate to the modified Hlavatý equation

$$x_2 = A_1 x_A \ln x_A + A_2 x_B \ln x_B + A_3 x_A x_B$$

The coefficients B_i relate to a β function

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

The coefficients C_i relate to a log γ equation

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

where

$$x_A = x_1 + (1/2)x_2 - x_1^0/(x_{11}^0 - x_1^0)$$

Table 2. Composition of Points on the Binodal Curve for the Mixtures $\{x_1\text{H}_2\text{O} + x_2\text{C}_0\text{H}_{2m+1}\text{OH} + (1 - x_1 - x_2)\text{1,4-NC(CH}_2)_4\text{CN or CH}_3\text{CH}_2\text{CH}_2\text{CN or C}_6\text{H}_5\text{CN}\}$ at $T = 298.15\text{ K}$

x_1	x_2	x_1	x_2	x_1	x_2
H ₂ O + CH ₃ OH + 1,4-NC(CH ₂) ₄ CN		H ₂ O + CH ₃ CH ₂ OH + 1,4-NC(CH ₂) ₄ CN		H ₂ O + CH ₃ CH ₂ CH ₂ OH + 1,4-NC(CH ₂) ₄ CN	
0.286	0.000	0.286	0.000	0.286	0.000
0.316	0.048	0.323	0.050	0.317	0.037
0.362	0.093	0.329	0.050	0.413	0.093
0.418	0.147	0.360	0.066	0.519	0.133
0.457	0.174	0.407	0.093	0.570	0.143
0.540	0.206	0.427	0.107	0.671	0.143
0.617	0.215	0.447	0.110	0.778	0.117
0.668	0.210	0.465	0.124	0.861	0.085
0.736	0.194	0.478	0.136	0.870	0.085
0.992	0.000	0.506	0.135	0.912	0.056
		0.545	0.148	0.948	0.036
		0.642	0.156	0.972	0.017
		0.682	0.154	0.992	0.000
		0.749	0.141		
		0.811	0.125		
		0.866	0.103		
		0.922	0.062		
		0.959	0.030		
		0.992	0.000		
H ₂ O + CH ₃ OH + CH ₃ CH ₂ CH ₂ CN		H ₂ O + CH ₃ CH ₂ OH + CH ₃ CH ₂ CH ₂ CN		H ₂ O + CH ₃ CH ₂ CH ₂ OH + CH ₃ CH ₂ CH ₂ CN	
0.096	0.096	0.096	0.000	0.096	0.000
0.123	0.134	0.134	0.081	0.137	0.071
0.163	0.232	0.232	0.146	0.193	0.122
0.249	0.312	0.312	0.187	0.258	0.175
0.329	0.405	0.405	0.211	0.358	0.224
0.415	0.525	0.525	0.216	0.441	0.245
0.511	0.624	0.624	0.198	0.547	0.245
0.524	0.737	0.737	0.166	0.645	0.218
0.583	0.754	0.754	0.163	0.699	0.195
0.654	0.814	0.814	0.136	0.764	0.160
0.698	0.874	0.874	0.101	0.844	0.112
0.723	0.913	0.913	0.071	0.846	0.111
0.775	0.958	0.958	0.031	0.928	0.056
0.791	1.000	1.000	0.000	0.951	0.037
0.876	0.108			0.975	0.016
0.919	0.068			1.000	0.000
0.962	0.028				
1.000	0.000				
H ₂ O + CH ₃ OH + C ₆ H ₅ CN		H ₂ O + CH ₃ CH ₂ OH + C ₆ H ₅ CN		H ₂ O + CH ₃ CH ₂ CH ₂ OH + C ₆ H ₅ CN	
0.054	0.000	0.054	0.000	0.054	0.000
0.071	0.080	0.093	0.116	0.073	0.086
0.106	0.156	0.150	0.189	0.117	0.167
0.132	0.208	0.208	0.244	0.172	0.212
0.224	0.336	0.301	0.290	0.199	0.270
0.283	0.379	0.406	0.316	0.295	0.303
0.339	0.404	0.522	0.304	0.350	0.330
0.414	0.418	0.549	0.301	0.437	0.345
0.545	0.397	0.612	0.280	0.541	0.325
0.565	0.391	0.659	0.266	0.745	0.212
0.648	0.333	0.707	0.241	0.746	0.210
0.655	0.324	0.809	0.178	0.810	0.164
0.746	0.249	0.896	0.103	0.874	0.114
0.818	0.180	0.934	0.065	0.943	0.055
0.887	0.113	0.969	0.030	0.962	0.037
0.931	0.068	1.000	0.000	0.981	0.018
0.965	0.034			1.000	0.000
1.000	0.000				

and

$$x_B = x_{11}^0 - x_1 - (1/2)x_2/(x_{11}^0 - x_1^0)$$

where x_1 refers to the mole fraction of water, x_2 refers to the mole fraction of the alkanol, and x_{11}^0 and x_1^0 refer to the mole fraction of water when the value of $x_2 = 0$. The coefficients A_i , B_i , and C_i are given in Table 5 together with the standard deviation, σ , which is defined as

$$\sigma = [\sum (x_{2,\text{calcd}} - x_{2,\text{exptl}})^2 / (n - 3)]^{1/2}$$

where n is the number of data points.

Tie Line Correlation. The NRTL model of Renon and Prausnitz⁷ and the UNIQUAC model of Abrams and Prausnitz⁸ were used to correlate the tie line data. The data were correlated using a computer program that minimized the objective function

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

where x_{kli} is the experimental composition of component i in phase l for the k th tie line and \bar{x}_{kli} is the calculated composition of component i in phase l for the k th tie line. n is the number of tie lines. When the NRTL equation was

Table 3. Composition of Conjugate Phases for the Mixtures $\{x_1\text{H}_2\text{O} + x_2\text{C}_m\text{H}_{2m+1}\text{OH} + (1 - x_1 - x_2)\text{1,4-NC(CH}_2)_4\text{CN or CH}_3\text{CH}_2\text{CH}_2\text{CN or C}_6\text{H}_5\text{CN}\}$ at $T = 298.15$ K and the Selectivity, S

x_{11}	x_{21}	x_{13}	x_{23}	S	x_{11}	x_{21}	x_{13}	x_{23}	S
H ₂ O + CH ₃ OH + 1,4-NC(CH ₂) ₄ CN									
0.992	0.000	0.285	0.000		0.821	0.149	0.395	0.126	1.8
0.941	0.052	0.319	0.050	2.9	0.766	0.180	0.419	0.148	1.5
0.912	0.079	0.342	0.074	2.5	0.650	0.216	0.460	0.176	1.2
0.875	0.111	0.367	0.099	2.1					
H ₂ O + CH ₃ CH ₂ OH + 1,4-NC(CH ₂) ₄ CN									
0.992	0.000	0.286	0.000		0.861	0.103	0.526	0.145	2.3
0.956	0.033	0.336	0.055	4.7	0.878	0.093	0.490	0.134	2.6
0.901	0.078	0.440	0.111	2.9					
H ₂ O + CH ₃ CH ₂ CH ₂ OH + 1,4-NC(CH ₂) ₄ CN									
0.992	0.000	0.286	0.000		0.915	0.056	0.600	0.146	3.9
0.960	0.026	0.420	0.097	8.4	0.897	0.067	0.677	0.142	2.8
0.931	0.046	0.557	0.141	5.1	0.876	0.078	0.741	0.128	1.9
H ₂ O + CH ₃ OH + CH ₃ CH ₂ CH ₂ CN									
1.000	0.000	0.096	0.000		0.827	0.149	0.191	0.136	4.0
0.909	0.077	0.118	0.060	6.0	0.800	0.170	0.213	0.157	3.5
0.874	0.109	0.143	0.089	5.0	0.640	0.251	0.283	0.215	1.9
0.839	0.139	0.177	0.123	4.2					
H ₂ O + CH ₃ CH ₂ OH + CH ₃ CH ₂ CH ₂ CN									
1.000	0.000	0.096	0.000		0.944	0.046	0.255	0.148	12
0.968	0.026	0.116	0.060	19	0.930	0.068	0.331	0.195	8.0
0.956	0.036	0.163	0.104	17	0.872	0.100	0.449	0.216	4.2
H ₂ O + CH ₃ CH ₂ CH ₂ OH + CH ₃ CH ₂ CH ₂ CN									
1.000	0.000	0.096	0.000		0.941	0.044	0.464	0.248	11
0.972	0.021	0.166	0.100	29	0.936	0.048	0.503	0.248	9.6
0.958	0.031	0.249	0.166	20	0.926	0.055	0.561	0.241	7.2
0.951	0.037	0.371	0.229	16					
H ₂ O + CH ₃ OH + C ₆ H ₅ CN									
1.000	0.000	0.054	0.000		0.755	0.242	0.089	0.123	4.3
0.932	0.066	0.062	0.044	10	0.683	0.301	0.103	0.153	3.4
0.857	0.142	0.067	0.064	5.7	0.576	0.373	0.129	0.202	2.4
0.809	0.190	0.074	0.085	4.9	0.503	0.404	0.146	0.232	2.0
0.786	0.212	0.080	0.100	4.6					
H ₂ O + CH ₃ CH ₂ OH + C ₆ H ₅ CN									
1.000	0.000	0.054	0.000		0.846	0.150	0.146	0.185	7.1
0.960	0.040	0.062	0.044	17	0.774	0.200	0.200	0.236	4.6
0.919	0.081	0.079	0.091	13	0.701	0.247	0.252	0.272	3.0
0.878	0.120	0.100	0.127	9.3					
H ₂ O + CH ₃ CH ₂ CH ₂ OH + C ₆ H ₅ CN									
1.000	0.000	0.054	0.000		0.957	0.041	0.252	0.288	26
0.978	0.021	0.084	0.111	60	0.950	0.047	0.283	0.304	22
0.964	0.034	0.161	0.218	38	0.949	0.048	0.352	0.332	19

Table 4. Composition of Plait Points for the Mixtures $\{x_1\text{H}_2\text{O} + x_2\text{C}_m\text{H}_{2m+1}\text{OH} + (1 - x_1 - x_2)\text{1,4-NC(CH}_2)_4\text{CN or CH}_3\text{CH}_2\text{CH}_2\text{CN or C}_6\text{H}_5\text{CN}\}$ at $T = 298.15$ K

	x_1	x_2
H ₂ O + CH ₃ OH + 1,4-NC(CH ₂) ₄ CN	0.560	0.215
H ₂ O + CH ₃ CH ₂ OH + 1,4-NC(CH ₂) ₄ CN	0.670	0.155
H ₂ O + CH ₃ CH ₂ CH ₂ OH + 1,4-NC(CH ₂) ₄ CN	0.818	0.102
H ₂ O + CH ₃ OH + CH ₃ CH ₂ CH ₂ CN	0.390	0.252
H ₂ O + CH ₃ CH ₂ OH + CH ₃ CH ₂ CH ₂ CN	0.696	0.181
H ₂ O + CH ₃ CH ₂ CH ₂ OH + CH ₃ CH ₂ CH ₂ CN	0.835	0.117
H ₂ O + CH ₃ OH + C ₆ H ₅ CN	0.213	0.329
H ₂ O + CH ₃ CH ₂ OH + C ₆ H ₅ CN	0.425	0.312
H ₂ O + CH ₃ CH ₂ CH ₂ OH + C ₆ H ₅ CN	0.735	0.217

fitted, the nonrandomness parameter α was set to 0.3. For the UNIQUAC correlation the pure component structural parameters (r , q , and q') were calculated by using the method outlined in the original paper by Abrams and Prausnitz⁸ and are given in Table 1. The resulting binary interaction parameters and the root-mean-square (rms) deviations are reported in Tables 6 and 7. The symbols and notation used are consistent with the original works by Renon and Prausnitz⁷ and Abrams and Prausnitz.⁸

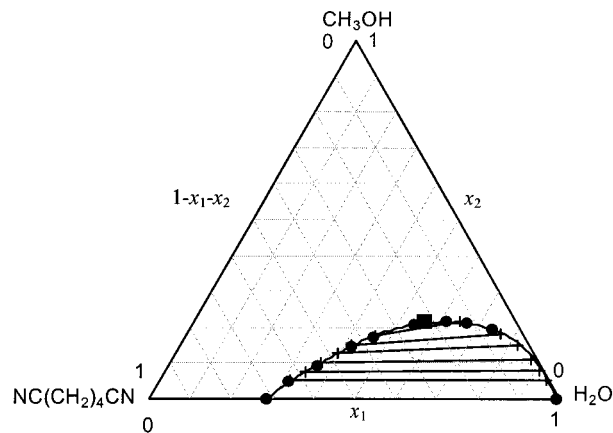


Figure 1. Liquid-liquid equilibrium results for the mixture $\{x_1\text{H}_2\text{O} + x_2\text{CH}_3\text{OH} + (1 - x_1 - x_2)\text{1,4-NC(CH}_2)_4\text{CN}\}$ at $T = 298.15$ K: ●, points on the binodal curve; +, points connecting conjugate phases; ■, critical or plait point.

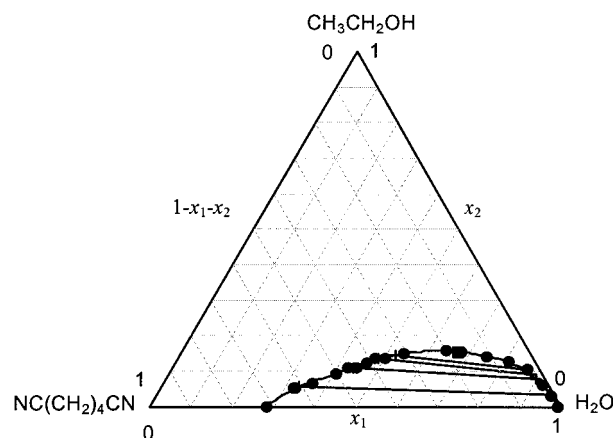


Figure 2. Liquid-liquid equilibrium results for the mixture $\{x_1\text{H}_2\text{O} + x_2\text{CH}_3\text{CH}_2\text{OH} + (1 - x_1 - x_2)\text{1,4-NC(CH}_2)_4\text{CN}\}$ at $T = 298.15$ K: ●, points on the binodal curve; +, points connecting conjugate phases; ■, critical or plait point.

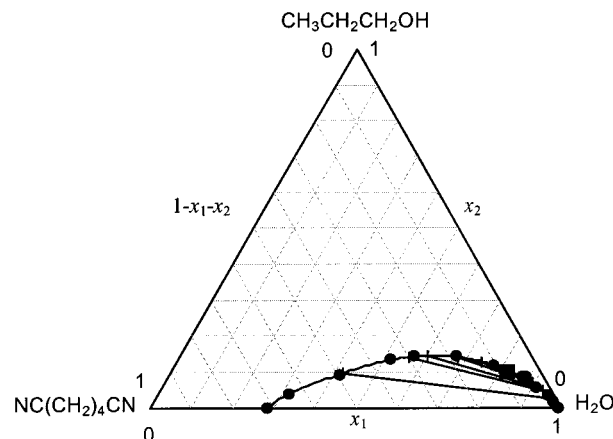


Figure 3. Liquid-liquid equilibrium results for the mixture $\{x_1\text{H}_2\text{O} + x_2\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + (1 - x_1 - x_2)\text{1,4-NC(CH}_2)_4\text{CN}\}$ at $T = 298.15$ K: ●, points on the binodal curve; +, points connecting conjugate phases; ■, critical or plait point.

Discussion

Previous Work. The only data reported in the literature for mixtures investigated in this work are the data presented for the mixtures $\{x_1\text{H}_2\text{O} + x_2\text{CH}_3\text{OH} + (1 - x_1 - x_2)\text{C}_6\text{H}_5\text{CN}\}$ at $T = 298.15$ K and data for the mixtures $\{x_1\text{H}_2\text{O} + x_2\text{CH}_3\text{CH}_2\text{OH} + (1 - x_1 - x_2)\text{C}_6\text{H}_5\text{CN}\}$ and

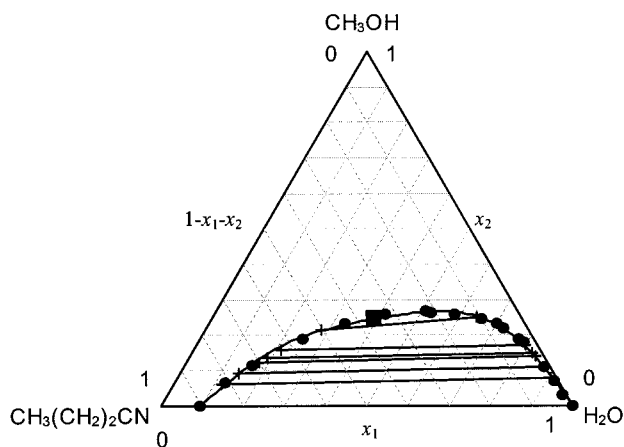


Figure 4. Liquid–liquid equilibrium results for the mixture $\{x_1\text{H}_2\text{O} + x_2\text{CH}_3\text{OH} + (1 - x_1 - x_2)\text{CH}_3(\text{CH}_2)_2\text{CN}\}$ at $T = 298.15$ K: ●, points on the binodal curve; +, points connecting conjugate phases; ■, critical or plait point.

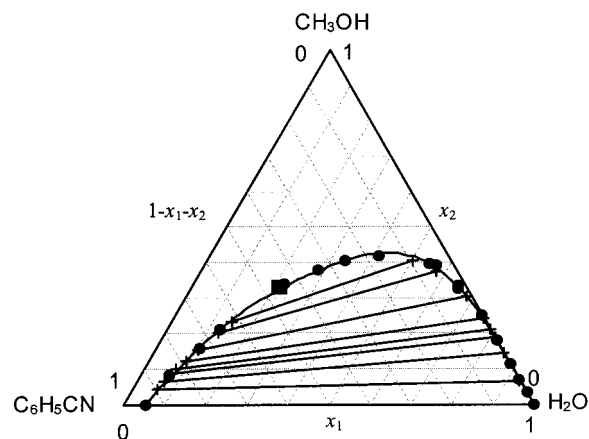


Figure 7. Liquid–liquid equilibrium results for the mixture $\{x_1\text{H}_2\text{O} + x_2\text{CH}_3\text{OH} + (1 - x_1 - x_2)\text{C}_6\text{H}_5\text{CN}\}$ at $T = 298.15$ K: ●, points on the binodal curve; +, points connecting conjugate phases; ■, critical or plait point.

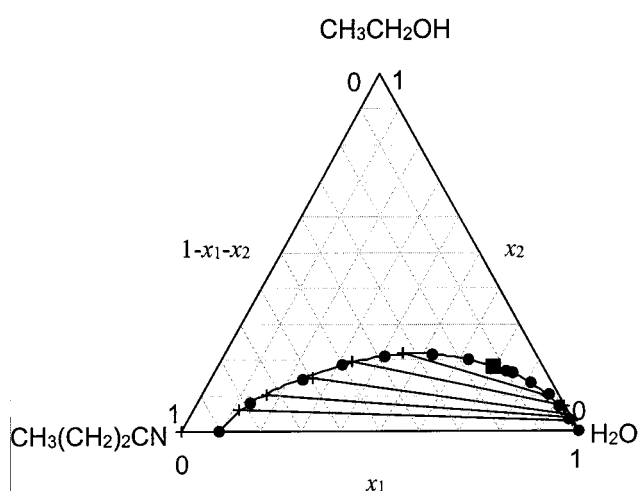


Figure 5. Liquid–liquid equilibrium results for the mixture $\{x_1\text{H}_2\text{O} + x_2\text{CH}_3\text{CH}_2\text{OH} + (1 - x_1 - x_2)\text{CH}_3(\text{CH}_2)_2\text{CN}\}$ at $T = 298.15$ K: ●, points on the binodal curve; +, points connecting conjugate phases; ■, critical or plait point.

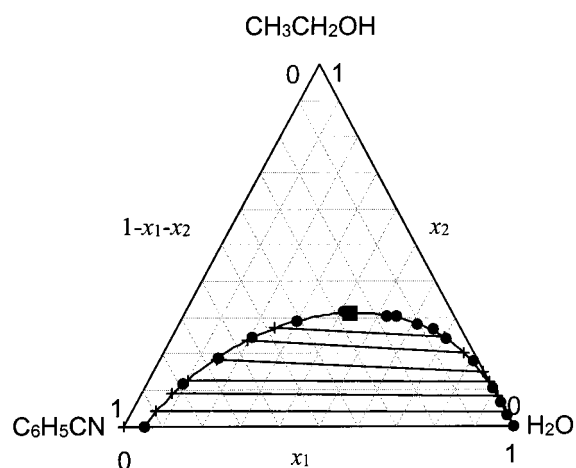


Figure 8. Liquid–liquid equilibrium results for the mixture $\{x_1\text{H}_2\text{O} + x_2\text{CH}_3\text{CH}_2\text{OH} + (1 - x_1 - x_2)\text{C}_6\text{H}_5\text{CN}\}$ at $T = 298.15$ K: ●, points on the binodal curve; +, points connecting conjugate phases; ■, critical or plait point.

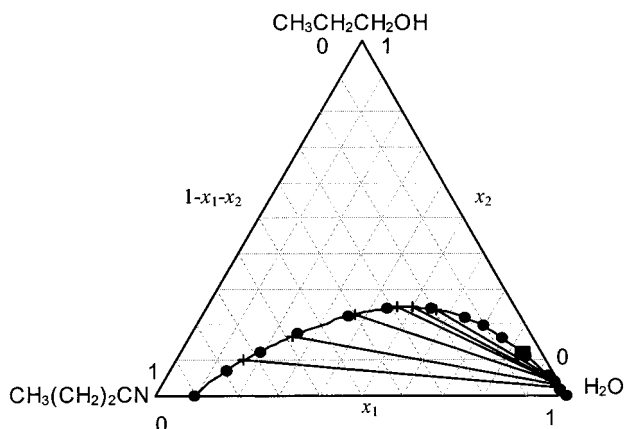


Figure 6. Liquid–liquid equilibrium results for the mixture $\{x_1\text{H}_2\text{O} + x_2\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + (1 - x_1 - x_2)\text{CH}_3(\text{CH}_2)_2\text{CN}\}$ at $T = 298.15$ K: ●, points on the binodal curve; +, points connecting conjugate phases; ■, critical or plait point.

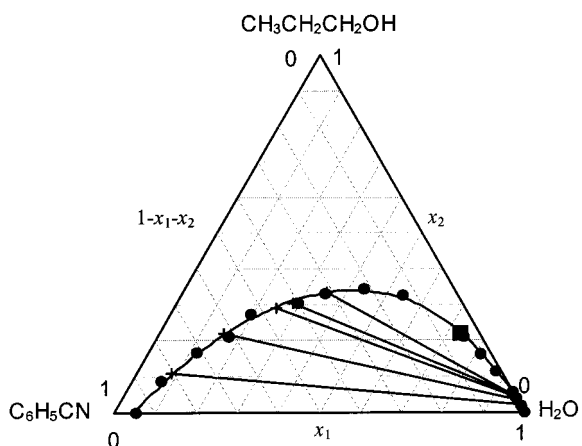


Figure 9. Liquid–liquid equilibrium results for the mixture $\{x_1\text{H}_2\text{O} + x_2\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + (1 - x_1 - x_2)\text{C}_6\text{H}_5\text{CN}\}$ at $T = 298.15$ K: ●, points on the binodal curve; +, points connecting conjugate phases; ■, critical or plait point.

$\{x_1\text{H}_2\text{O} + x_2\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + (1 - x_1 - x_2)\text{C}_6\text{H}_5\text{CN}\}$ at $T = 298.15$ K. Grande et al.³ and Botto et al.⁴ used the direct analytical method. In both cases gas–liquid chromatography was used to determine the composition of the conjugate phases. The literature results report a precision of 0.002

mole fraction. The literature data and the results of this work are in agreement to within 0.055 in the worst case. The most probable reason for this difference is that the alkanols used by Grande et al.³ and by Botto et al.⁴ contained water as their work did not report the results of a moisture analysis.

Table 5. Hlavatý, β , and $\log \gamma$ Parameters and Their Standard Deviations for Mixtures $\{x_1\text{H}_2\text{O} + x_2\text{C}_m\text{H}_{2m+1}\text{OH} + (1 - x_1 - x_2)1,4\text{-NC}(\text{CH}_2)_4\text{CN or CH}_3\text{CH}_2\text{CH}_2\text{CN or C}_6\text{H}_5\text{CN}\}$ at $T = 298.15\text{ K}$

	A_1	A_2	A_3	σ	B_1	B_2	B_3	σ	C_1	C_2	C_3	σ
$\text{H}_2\text{O} + \text{CH}_3\text{OH} + 1,4\text{-NC}(\text{CH}_2)_4\text{CN}$	-0.012	-0.548	0.044	0.001	0.598	0.581	0.975	0.001	0.550	0.535	1.158	0.002
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{OH} + 1,4\text{-NC}(\text{CH}_2)_4\text{CN}$	-0.067	-0.399	-0.047	0.003	0.488	0.711	0.965	0.005	0.458	0.690	1.223	0.005
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 1,4\text{-NC}(\text{CH}_2)_4\text{CN}$	-0.013	-0.233	0.024	0.002	0.491	0.793	0.971	0.003	0.462	0.775	1.260	0.004
$\text{H}_2\text{O} + \text{CH}_3\text{OH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$	0.0002	-0.454	0.433	0.009	1.221	0.955	1.112	0.016	1.128	0.928	1.456	0.017
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$	-0.150	-0.356	0.158	0.004	0.785	0.848	0.939	0.008	0.734	0.825	1.251	0.009
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$	0.135	-0.127	0.995	0.005	1.170	1.030	1.147	0.008	1.091	1.009	1.533	0.009
$\text{H}_2\text{O} + \text{CH}_3\text{OH} + \text{C}_6\text{H}_5\text{CN}$	0.318	-0.401	1.544	0.014	1.950	0.991	1.171	0.019	1.801	0.965	1.530	0.021
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{CN}$	-0.092	-0.498	0.437	0.005	1.251	0.878	1.040	0.010	1.188	0.863	1.378	0.011
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{CN}$	0.037	-0.286	0.999	0.007	1.434	0.943	1.108	0.008	1.378	0.933	1.491	0.010

Table 6. NRTL Binary Interaction Parameters and the Root-Mean-Square Deviations (rms) for the Mixtures^a $\{x_1\text{H}_2\text{O} + x_2\text{C}_m\text{H}_{2m+1}\text{OH} + (1 - x_1 - x_2)1,4\text{-NC}(\text{CH}_2)_4\text{CN or CH}_3(\text{CH}_2)_2\text{CN or C}_6\text{H}_5\text{CN}\}$ ^b

	$\frac{g_{12} - g_{22}}{\text{J mol}^{-1}}$	$\frac{g_{21} - g_{11}}{\text{J mol}^{-1}}$	$\frac{g_{13} - g_{33}}{\text{J mol}^{-1}}$	$\frac{g_{31} - g_{11}}{\text{J mol}^{-1}}$	$\frac{g_{23} - g_{33}}{\text{J mol}^{-1}}$	$\frac{g_{32} - g_{22}}{\text{J mol}^{-1}}$	rms
$\text{H}_2\text{O} + \text{CH}_3\text{OH} + 1,4\text{-NC}(\text{CH}_2)_4\text{CN}$	7141	-3218	11578	1715	1712	2265	0.011
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{OH} + 1,4\text{-NC}(\text{CH}_2)_4\text{CN}$	4477	-3551	11561	1702	-297	208	0.007
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 1,4\text{-NC}(\text{CH}_2)_4\text{CN}$	9768	-3112	8693	1723	2288	320	0.013
$\text{H}_2\text{O} + \text{CH}_3\text{OH} + \text{CH}_3(\text{CH}_2)_2\text{CN}$	3240	-1710	12149	4560	1014	1992	0.014
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3(\text{CH}_2)_2\text{CN}$	9682	-2331	8765	4636	4582	326	0.014
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_3(\text{CH}_2)_2\text{CN}$	9825	-2113	9090	4326	4534	301	0.008
$\text{H}_2\text{O} + \text{CH}_3\text{OH} + \text{C}_6\text{H}_5\text{CN}$	1432	-190	16657	6869	3247	1630	0.010
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{CN}$	911	1840	13480	13165	1525	1049	0.014
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{CN}$	8811	-998	10986	5996	3631	1564	0.007

^a $\alpha = 0.3$. ^b Subscripts 1, 2, and 3 indicate water, the alkanol, and the nitrile compound, respectively.

Table 7. UNIQUAC Binary Interaction Parameters and the Root-Mean-Square Deviations (rms) for the Mixtures $\{x_1\text{H}_2\text{O} + x_2\text{C}_m\text{H}_{2m+1}\text{OH} + (1 - x_1 - x_2)1,4\text{-NC}(\text{CH}_2)_4\text{CN or CH}_3(\text{CH}_2)_2\text{CN or C}_6\text{H}_5\text{CN}\}$ ^a

	$\frac{u_{12} - u_{22}}{\text{J mol}^{-1}}$	$\frac{u_{21} - u_{11}}{\text{J mol}^{-1}}$	$\frac{u_{13} - u_{33}}{\text{J mol}^{-1}}$	$\frac{u_{31} - u_{11}}{\text{J mol}^{-1}}$	$\frac{u_{23} - u_{33}}{\text{J mol}^{-1}}$	$\frac{u_{32} - u_{22}}{\text{J mol}^{-1}}$	rms
$\text{H}_2\text{O} + \text{CH}_3\text{OH} + 1,4\text{-NC}(\text{CH}_2)_4\text{CN}$	-327	-325	25	450	69	266	0.016
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{OH} + 1,4\text{-NC}(\text{CH}_2)_4\text{CN}$	32	-6	-30	525	-264	1906	0.011
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 1,4\text{-NC}(\text{CH}_2)_4\text{CN}$	5	4	-75	664	-360	1675	0.028
$\text{H}_2\text{O} + \text{CH}_3\text{OH} + \text{CH}_3(\text{CH}_2)_2\text{CN}$	88	-424	151	553	15	-84	0.013
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3(\text{CH}_2)_2\text{CN}$	8	-231	76	710	-493	621	0.019
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_3(\text{CH}_2)_2\text{CN}$	336	-187	62	640	-58	-442	0.012
$\text{H}_2\text{O} + \text{CH}_3\text{OH} + \text{C}_6\text{H}_5\text{CN}$	117	-373	52	672	-30	338	0.019
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{CN}$	-638	225	4	4540	-17	-283	0.018
$\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{CN}$	332	-218	57	800	-45	-351	0.010

^a Subscripts 1, 2, and 3 indicate water, the alkanol, and the nitrile compound, respectively.

This Work. The mixtures (water + an alkanol + a nitrile compound) were studied to determine the suitability of a nitrile compound for separating water–alkanol mixtures. Three nitrile compounds were chosen for this investigation, namely, 1,4-NC(CH₂)₄CN, CH₃(CH₂)₂CN, and C₆H₅CN. The reason for choosing these nitrile compounds was to investigate the effect of the nitrile functionality in three different types of molecule (a simple nitrile compound, a nitrile with two terminal nitrile groups, and a nitrile group attached to benzene) on the phase separation of water–alkanol mixtures. Three alkanols, namely, methanol, ethanol, and propanol, were investigated to determine the effect that an increase in the carbon chain number of the alkanol had on the phase separation of water–alcohol mixtures.

The area of the two-phase region for the mixtures (water + an alkanol + 1,4-dicyanobutane or butanenitrile or benzonitrile) is small. This indicates the reasonably high mutual solubility of the components of the mixture. As the number of carbon atoms in the alkanol increases from 1 to 3 there is a small decrease in the area of the two-phase region for the mixtures (water + an alkanol + 1,4-dicyanobutane or butanenitrile or benzonitrile) at $T = 298.15\text{ K}$. The decrease in the two-phase region as the carbon atoms in the alkanol increases from 1 to 3 indicates that the mutual solubility of the components increases as the carbon chain length of the alkanol increases.

The slope of the tie lines (see Figures 1–9) indicates that the solubility of the alkanol in the nitrile compound increases as the carbon chain length of the alkanol increases from 1 to 3. This is also reflected in Figure 10, which shows the distribution of the alkanol in the water-rich phase and in the nitrile compound-rich phase. This indicates that it is possible to separate methanol–ethanol or methanol–propanol mixtures by partitioning the alkanols between water and a nitrile compound.

The areas of the two-phase region for the mixtures (water + an alkanol + a nitrile compound) are small. Unfortunately, this indicates that the nitrile compounds are effective as liquid–liquid extraction solvents for the separation of water–alkanol mixtures only over a small concentration range.

The vapor pressure of benzonitrile is very much less than the vapor pressures of the alkanols or water; hence, it will be easy to recover benzonitrile using distillation from mixtures with alkanols or water after the initial liquid–liquid extraction.

The NRTL and UNIQUAC models are able to model the tie line data relatively well, with the NRTL model being the better of the two. This is most likely due to the fact that the NRTL model is a three-parameter model and the UNIQUAC model is a two-parameter model. A comparison of the fit of both these models to the data presented

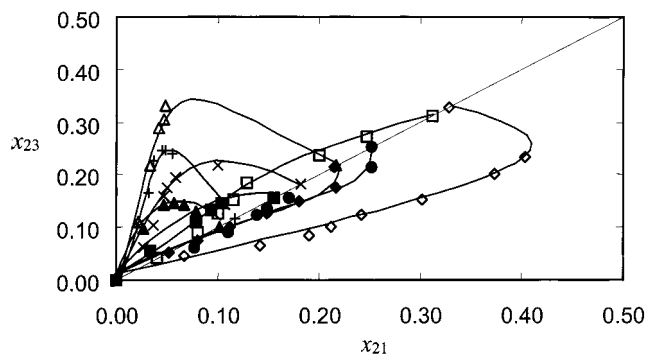


Figure 10. Distribution of the alkanol between the water-rich phase and the nitrile compound-rich phase at $T = 298.15$ K; x_{21} and x_{23} are the concentration of the alkanol in the water-rich phase and the concentration of the alkanol in the nitrile compound-rich phase, respectively: \blacklozenge , $\text{H}_2\text{O} + \text{CH}_3\text{OH} + 1,4\text{-NC}(\text{CH}_2)_4\text{CN}$; \blacksquare , $\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{OH} + 1,4\text{-NC}(\text{CH}_2)_4\text{CN}$; \blacktriangle , $\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 1,4\text{-NC}(\text{CH}_2)_4\text{CN}$; \bullet , $\text{H}_2\text{O} + \text{CH}_3\text{OH} + \text{CH}_3(\text{CH}_2)_2\text{CN}$; \times , $\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3(\text{CH}_2)_2\text{CN}$; $+$, $\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_3(\text{CH}_2)_2\text{CN}$; \diamond , $\text{H}_2\text{O} + \text{CH}_3\text{OH} + \text{C}_6\text{H}_5\text{CN}$; \square , $\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{CN}$; \triangle , $\text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{CN}$.

in this work to the fit of the models to data presented previously for the mixtures (an alkane + an aromatic hydrocarbon + 1,4-dicyanobutane) at $T = 298.15$ K¹ shows that the models do not perform as well here. This is probably due to the presence of hydrogen bonds, which are found in the mixtures investigated in this work. The models were originally designed to account for weak intermolecular interactions and not interactions such as hydrogen bonding.

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