J. Chem. Eng. Data **1999,** *44,* 1178−1182

Ternary Liquid−Liquid Equilibria for Mixtures of Quinoline + an Alkanol + Water at 298.2 K and 1 atm

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The binodal curves and liquid−liquid equilibrium data are presented for mixtures of (quinoline + an alkanol + water) at 298.2 K. The alkanols used were methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methylpropan-1-ol, and 2-methylpropan-2-ol. The solubility of the alkanols is higher in the quinoline layer than in the water layer. The results have been fitted to Hlavatý's equation, the β density function, and the logarithmic γ function. The binodal curves obtained from these equations have been compared with the experimental binodal curves. The NRTL equation was also used to correlate the experimental tie lines. There are no data in the literature for the mixtures discussed in this paper. The effectiveness of the extraction of an alkanol by quinoline is reported as a ratio of the solubilities in the two phases.

Introduction

In previous studies by Letcher and co-workers (1986, 1989, 1990, 1992) measurements were made for mixtures of (an alkanol + an aliphatic or an aromatic compound + water), where the alkanol refers to methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methylpropan-1-ol, and 2-methylpropan-2-ol. This work extends the previously reported work by including a heterocyclic compound, namely quinoline.

The purpose of this work is to determine the binodal curve and the precise tie lines for the ternary mixtures detailed above, to investigate the possibility of separating alkanols using liquid−liquid extraction.

Liquid−liquid extraction is often more acceptable than distillation as a technique for separating liquids because it does not involve a heating process. The liquid−liquid extraction solvent, however, should have a low vapor pressure (so as not to contaminate the environment). Quinoline is one such solvent, and its potential in separating aqueous mixtures of alkanols is the subject of this paper.

Experimental Section

Procedure. The binodal curves were determined at 298.2 K and 1 atm pressure using the cloud point method described by Letcher and Siswana (1992). The precision of the technique was better than 0.002 mole fraction. Tie lines were determined using the refractive index method described by Briggs and Comings (1943). Plait points were determined following the method of Treybal (1946). The precision of the technique in determining the composition of the tie lines was better than 0.01 mole fraction.

The refractive indices, molar volumes, suppliers, and purity of the pure compounds at 298.2 K are given in Table 1. The C1−C2 alkanols were dried with calcium hydride, the C3 alkanols were dried with anhydrous potassium carbonate, and the C4 alkanols were dried by the addition of anhydrous potassium carbonate. Karl Fischer titrations were done on all the alkanols, and the percentage of water was found to be <0.1%. Quinoline was first dried by the addition of potassium iodide, followed by distillation. The quinoline was purified on the same day as each experiment was conducted and was tested for water contamination. Impurities (less than 0.5%) other than water (always less than 0.1%) were not known.

Table 1. Refractive Index n_D and Molar Volumes V_m at 298.2 K for the Compounds Used in This Work

compound	refractive index n_D lit.[a]	exp	V_m/(cm^3·mol^{-1})	supplier	purity (%)
methanol	1.3263	1.3265	43.29	Labscan	>99
ethanol	1.3594	1.3592	58.69	Riedel de Haen	99
1-propanol	1.3837	1.3824	75.15	Riedel de Haen	>99
2-propanol	1.3752	1.3752	76.92	Merck	99
1-butanol	1.3974	1.3957	91.99	Janssen Chimica	99
2-butanol	1.3953	1.3959	92.37	Merck	99
2-methyl-propan-1-ol	1.3928	1.3963	92.91	Acros	99
2-methyl-propan-2-ol	1.3852	1.3852	94.88	Acros	99
quinoline	1.6268	1.6234	118.52	Univar	99
water	1.3325	1.3325	18.07		

[a] Riddick et al. (1986).

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 compositions of the plait points determined following the method of Treybal et al. (1946) are given in Table 4. The binodal curves and tie line results have been plotted in Figure 1. The relative solubilities of the alkanols in quinoline and water have been plotted in Figure 2. Three equations have been fitted to these data following the work of Hlavatý (1972). The coefficients A_I relate to a modified Hlavatý equation

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

The coefficients B_i relate to a β function equation

$$x_2 = B_2(1 - x_A)^{B1} x_A{}^{B2} \qquad (2)$$

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10.1021/je9900934 CCC: $18.00

Table 2. Composition of Points on the Coexistence Curve at 298.2 K for Mixtures Quinoline (1) + an Alkanol (2) + Water (3)

methanol		ethanol		1-propanol		2-propanol	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.006
0.002	0.108	0.000	0.003	0.001	0.045	0.000	0.035
0.014	0.204	0.001	0.153	0.002	0.051	0.002	0.064
0.038	0.229	0.001	0.162	0.003	0.065	0.002	0.055
0.062	0.242	0.032	0.273	0.012	0.103	0.009	0.076
0.069	0.245	0.068	0.306	0.020	0.129	0.027	0.107
0.170	0.256	0.132	0.305	0.031	0.235	0.069	0.154
0.203	0.224	0.138	0.306	0.058	0.259	0.120	0.182
0.204	0.218	0.139	0.301	0.066	0.269	0.123	0.182
0.213	0.217	0.143	0.302	0.101	0.266	0.139	0.186
0.227	0.211	0.153	0.293	0.101	0.266	0.154	0.190
0.230	0.206	0.168	0.286	0.177	0.239	0.204	0.177
0.251	0.184	0.179	0.278	0.241	0.197	0.245	0.149
0.251	0.190	0.207	0.265	0.275	0.170	0.269	0.141
0.260	0.184	0.214	0.254	0.377	0.076	0.322	0.127
0.300	0.134	0.231	0.254	0.422	0.000	0.333	0.090
0.313	0.130	0.271	0.209			0.337	0.087
0.338	0.099	0.294	0.177			0.391	0.066
0.352	0.070	0.298	0.170			0.422	0.000
0.409	0.014	0.399	0.024				
0.417	0.010	0.407	0.010				
0.421	0.001	0.422	0.000				
0.421	0.002						
0.422	0.000						

1-butanol		2-butanol		2-methyl-propan-1-ol		2-methyl-propan-2-ol	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.000	0.018	0.000	0.056	0.000	0.025	0.000	0.013
0.000	0.501	0.001	0.000	0.000	0.562	0.013	0.078
0.001	0.000	0.000	0.312	0.001	0.000	0.015	0.080
0.003	0.024	0.051	0.318	0.000	0.011	0.043	0.140
0.047	0.477	0.096	0.306	0.013	0.551	0.083	0.184
0.048	0.468	0.128	0.292	0.034	0.533	0.108	0.205
0.074	0.465	0.142	0.299	0.069	0.497	0.117	0.200
0.090	0.434	0.146	0.291	0.084	0.485	0.146	0.196
0.130	0.398	0.150	0.300	0.099	0.478	0.175	0.186
0.183	0.351	0.202	0.247	0.100	0.476	0.214	0.168
0.282	0.204	0.207	0.249	0.127	0.449	0.233	0.160
0.307	0.178	0.270	0.182	0.150	0.421	0.250	0.147
0.325	0.141	0.294	0.162	0.155	0.415	0.289	0.122
0.336	0.148	0.298	0.168	0.196	0.374	0.296	0.121
0.355	0.114	0.338	0.124	0.208	0.360	0.335	0.083
0.405	0.032	0.352	0.089	0.255	0.278	0.361	0.055
0.422	0.000	0.422	0.000	0.289	0.217	0.422	0.000
				0.329	0.168		
				0.333	0.153		
				0.371	0.102		
				0.382	0.085		
				0.401	0.053		
				0.422	0.000		

and the coefficient C_i relates to a log γ equation

$$x_2 = C_1(-\ln x_A)^{C2} x_A{}^{C3} \tag{3}$$

where

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

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

and x_1 refers to the mole fraction composition of the quinoline, x_2 refers to the mole fraction of an alkanol, 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.

Table 3. Compositions of the Conjugate Solutions x_1', x_2' and x_1'', x_2'' at 298.2 K for the System Quinoline (1) + Alkanol (2) + Water (3)

water-rich phase		quinoline-rich phase	
x_1'	x_2'	x_1''	x_2''
	Methanol		
0.012	0.019	0.415	0.013
0.012	0.019	0.384	0.038
0.022	0.039	0.324	0.120
0.024	0.042	0.217	0.215
0.058	0.110	0.169	0.241
	Ethanol		
0.001	0.010	0.403	0.039
0.001	0.022	0.367	0.085
0.005	0.044	0.212	0.256
0.005	0.050	0.139	0.307
0.005	0.053	0.085	0.315
0.013	0.133	0.069	0.307
	1-Propanol		
0.001	0.009	0.403	0.039
0.000	0.003	0.346	0.111
0.002	0.014	0.327	0.135
0.002	0.017	0.232	0.237
0.003	0.026	0.055	0.266
	2-Propanol		
0.007	0.075	0.121	0.178
0.006	0.070	0.176	0.185
0.005	0.063	0.232	0.186
0.003	0.054	0.348	0.092
0.000	0.035	0.393	0.045
	1-Butanol		
0.000	0.009	0.048	0.479
0.000	0.008	0.072	0.459
0.000	0.012	0.075	0.456
0.000	0.008	0.153	0.374
0.000	0.014	0.317	0.164
	2-Butanol		
0.000	0.005	0.390	0.046
0.000	0.007	0.364	0.070
0.000	0.007	0.364	0.172
0.001	0.010	0.340	0.200
0.002	0.011	0.211	0.269
0.003	0.021	0.121	0.315
	2-Methylpropan-1-ol		
0.000	0.011	0.386	0.073
0.000	0.011	0.271	0.255
0.000	0.012	0.176	0.392
0.001	0.012	0.156	0.418
0.011	0.021	0.048	0.531
	2-Methylpropan-2-ol		
0.009	0.044	0.389	0.037
0.011	0.057	0.183	0.184
0.012	0.059	0.154	0.194
0.012	0.063	0.117	0.198
0.015	0.076	0.131	0.197

Table 4. Compositions of Plait Points for the Mixtures (Quinoline + an Alkanol + Water) at 298.2 K and 1 atm Pressure where x_1 and x_2 are the Mole Fractions of Quinoline and an Alkanol, Respectively

alkanol	x_1	x_2
methanol	0.144	0.245
ethanol	0.051	0.262
1-propanol	0.103	0.256
2-propanol	0.091	0.164
2-methylpropan-2-ol	0.052	0.145

These equations have been used to correlate the binodal curve. The coefficients A_i , B_i, and C_i are given in Table 5 together with the standard deviation σ, which is defined as

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

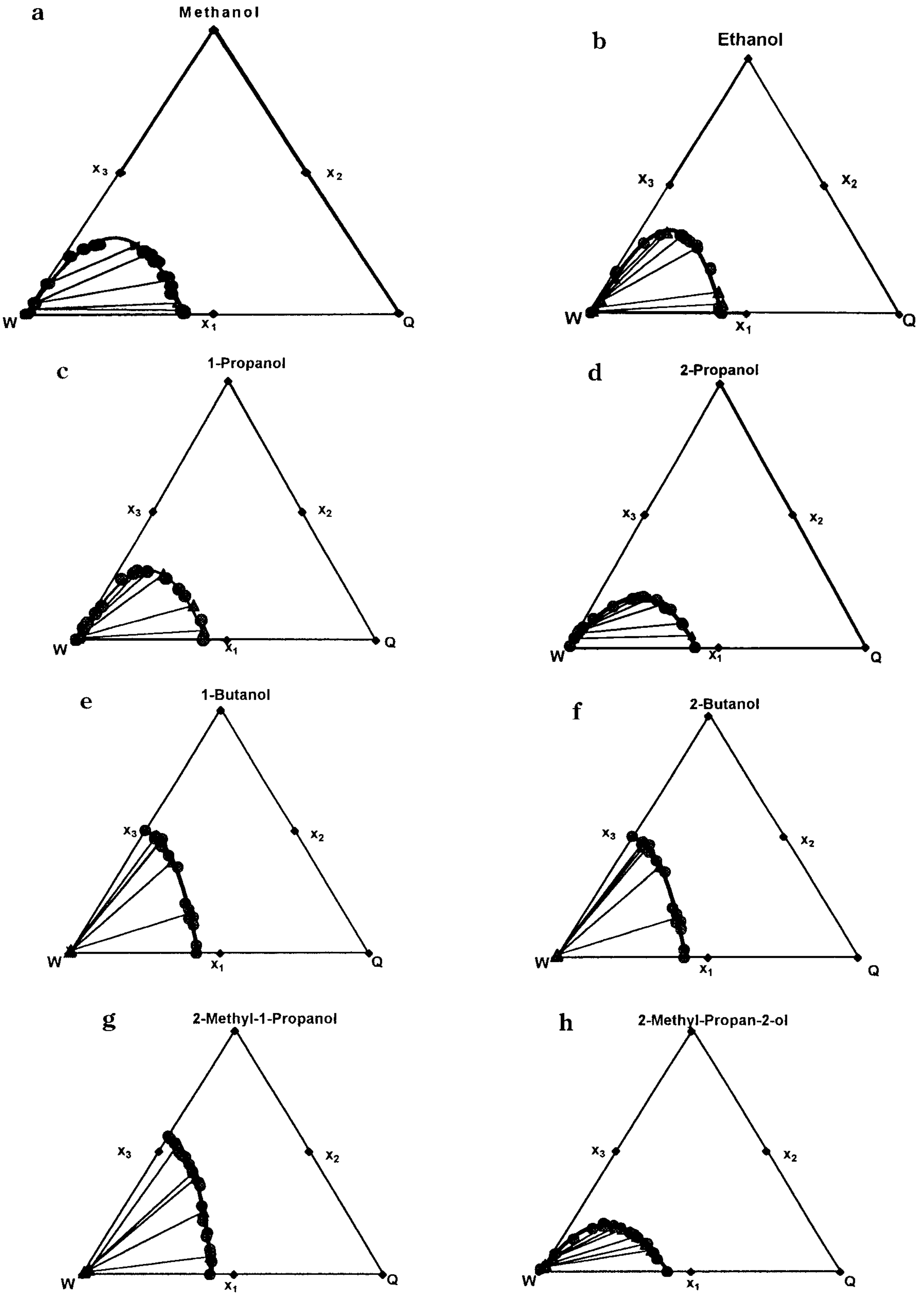

Figure 1. Binodal curves and tie lines for quinoline (Q) (1) + an alkanol (2) + water (W) (3) at 298.2 K: (a) methanol; (b) ethanol; (c) 1-propanol; (d) 2-propanol; (e) 1-butanol; (f) 2-butanol; (g) 2-methylpropan-1-ol; (h) 2-methylpropan-2-ol. x_1, x_2, and x_3 are mole fractions.

where n is the number of data points and 3 is the number of coefficients.

Discussion

Previous work by Letcher (1989) indicated that the shape of the binodal curve is very much dependent on the type of alkanol. This has also been found to be the case in this work. The minimum concentration (in mole fraction) for the alcohol solubility, over the whole composition range, in the quinoline−water system was found to be 0.25, 0.26, 0.28, 0.35, and 0.43 for 2-propanol, 1-propanol, ethanol, methanol, and 1-butanol, respectively.

From the slope of the tie lines (see Figure 1), it can be seen that, in all cases, the alkanols are more soluble in

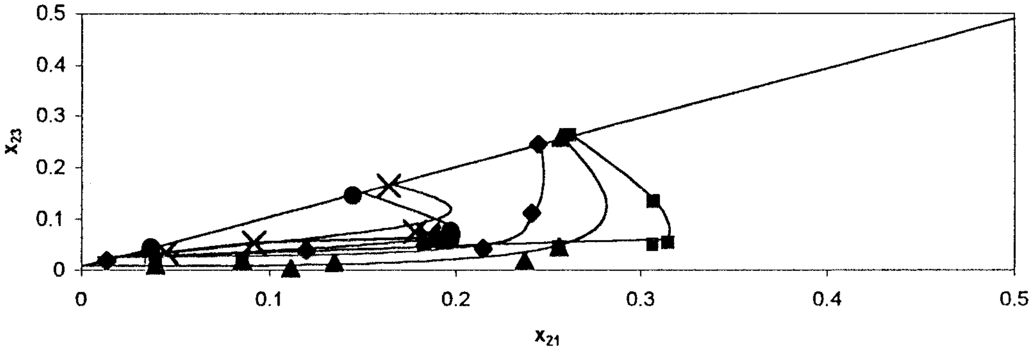

Figure 2. Relative solubility of an alkanol (2) in quinoline (1) and water (3), respectively, at 298.2 K and 1 atm pressure: x_{21} versus x_{23}. Legend: (■) ethanol; (▲) 1-propanol; (◆) methanol; (×) 2-propanol; (●) 2-methylpropan-2-ol.

Table 5. Coefficients A_1, A_2, A_3, B_1, B_2, B_3, C_1, C_2, and C_3 in Eqs 1, 2, and 3 together with the Standard Errors and the Standard Deviation σ, Using the Experimental and Calculated x_2 Values at 298.2 K for the Mixtures Quinoline (1) + an Alkanol (2) + Water (3)

solute	A_1	A_2	A_3	σ
methanol	0.142	−0.194	0.994	0.025
ethanol	−0.184	−0.839	−0.225	0.008
1-propanol	0.087	−0.358	0.677	0.026
2-propanol	−0.126	−0.327	0.102	0.013
1-butanol	0.558	−0.189	2.506	0.008
2-butanol	−0.377	−0.516	0.028	0.007
2-methylpropan-1-ol	0.632	−0.170	2.711	0.014
2-methylpropan-2-ol	0.088	−0.043	0.854	0.017
solute	B_1	B_2	B_3	σ
methanol	1.100	0.913	1.128	0.025
ethanol	1.077	0.710	1.142	0.011
1-propanol	0.912	0.767	1.038	0.021
2-propanol	0.501	0.656	0.816	0.011
1-butanol	2.405	0.983	1.346	0.009
2-butanol	0.927	0.734	0.818	0.007
2-methylpropan-1-ol	0.811	0.583	0.171	0.009
2-methylpropan-2-ol	0.826	0.975	1.087	0.016
solute	C_1	C_2	C_3	σ
methanol	1.142	0.933	1.596	0.033
ethanol	1.055	0.703	1.450	0.011
1-propanol	0.848	0.735	1.312	0.025
2-propanol	0.466	0.621	1.045	0.012
1-butanol	2.258	0.962	1.709	0.010
2-butanol	0.913	0.729	1.145	0.007
2-methylpropan-1-ol	0.828	0.466	0.201	0.009
2-methylpropan-2-ol	0.828	0.981	1.543	0.011

the quinoline-rich phase than the water-rich phase, with a large skewing toward the water axis.

The results for fitting the binodal curve data to the Hlavatý eq (1972) and the β density function (Letcher et al., 1990) and the logarithmic γ function (Letcher et al., 1990) show good correlation, as was found previously for other mixtures (Letcher and Siswana, 1989).

The area of the two-phase region increases in the order 2-propanol < 2-methylpropan-2-ol < methanol < 1-propanol < ethanol < 2-butanol < 1-butanol < 2-methylpropan-1-ol, with 1-butanol, 2-butanol, and 2-methylpropan-1-ol exhibiting a type II behavior and the remaining five systems a type I behavior. The maximum solubility of water in quinoline as given in the literature is 0.43 mole fraction at 298.2 K (extrapolated from the data of Zegalska, 1968), and the maximum solubility of quinoline in water is 0.0009 mole fraction at 293.2 K (also extrapolated from the data of Zegalska, 1968). Our work shows a maximum solubility of water in quinoline of 0.422 mole fraction at 298.2 K and a maximum solubility of quinoline in water of less than 0.001 mole fraction at 298.2 K.

Table 6. Values of the Parameters for the NRTL Equations, Determined from Ternary Liquid−Liquid Equilibrium Data for the Mixtures [Quinoline (1) + Alkanol (2) + Water (3)] at 298.2 K, as Well as the rmsd Values

component	NRTL[a] parameter (J·mol^{-1})			
$i{-}j$	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$
	Methanol** (0.006)		Ethanol (0.016)	
1−2 2−1	5473.28	3930.39	3247.43	1618.71
1−3 3−1	−287.58	10879.46	1548.99	6198.13
2−3 3−2	1665.04	7980.94	11934.87	5202.94
	1-Propanol (0.016)		2-Propanol (0.018)	
1−2 2−1	2389.21	1665.42	4333.57	1247.37
1−3 3−1	7483.71	7202.71	1728.93	6490.53
2−3 3−2	7665.68	5601.51	7306.82	4161.63
	1-Butanol* (0.002)		2-Butanol (0.013)	
1−2 2−1	3110.27	4002.12	17227.85	−4002.43
1−3 3−1	2054.83	14277.06	5387.23	7002.39
2−3 3−2	1816.42	9636.90	9498.34	5773.19
	2-Methylpropan-1-ol* (0.003)		2-Methylpropan-2-ol* (0.001)	
1−2 2−1	2368.46	3379.60	5317.70	4669.99
1−3 3−1	994.48	11704.04	874.84	11585.55
2−3 3−2	2827.86	8529.31	−865.93	9042.54

[a] Calculated with $\alpha_{ij} = 0.45$ and $\alpha_{ij} = 0.40$ (*) and $\alpha_{ij} = 0.35$ (**). The rms deviations are given in parentheses.

The literature data for the maximum solubility of water in 1-butanol, 2-butanol, and 2-methyl-1-propanol at 298.2 K are 0.518, 0.671, and 0.450, respectively (Kwertes, 1984). Our results for the same binary mixtures are 0.499, 0.688, and 0.438, respectively. The maximum solubility of alkanol in water at 298.2 K for the alkanols 1-butanol, 2-butanol, and 2-methylpropan-1-ol is 0.018, 0.050, and 0.021, respectively (Kwertes, 1984). Our results for the same binary mixtures are 0.019, 0.056, and 0.025, respectively.

The thermodynamic model the nonrandom two-liquid equation (NRTL equation) (Renon and Prausnitz, 1968) was used to correlate the experimental data for all the mixtures reported here. The equations and algorithms used in the calculation of the compositions of the liquid phases follow the method used by Walas (1985). The objective function $F(P)$, used to minimize the difference between the experimental and calculated concentrations is defined as

$$F(P) = \sum_{i=1}^{n} [x'_{1i} - x'_{1i}(\text{calc})]^2 + [x'_{2i} - x'_{2i}(\text{calc})]^2 + [x''_{1i} - x''_{1i}(\text{calc})]^2 + [x''_{2i} - x''_{2i}(\text{calc})]^2 \quad (7)$$

where P is the set of parameters vector, n is the number

Table 7. Representative Selectivity Values (*S*) and the Respective Tie Line Composition at 298.2 K for the System Quinoline (1) + Alkanol (2) + Water (3)

solute	selectivity (*S*)	tie line composition			
		water-rich phase		quinoline-rich phase	
		x'_1	x'_2	x''_1	x''_2
methanol	8	0.024	0.042	0.217	0.215
ethanol	11	0.005	0.050	0.139	0.307
1-propanol	76	0.000	0.003	0.346	0.111
2-propanol	5	0.005	0.063	0.232	0.186
1-butanol	124	0.000	0.008	0.072	0.459
2-butanol	56	0.000	0.007	0.364	0.172
2-methylpropan-1-ol	82	0.001	0.012	0.156	0.418
2-methylpropan-2-ol	5	0.011	0.057	0.183	0.184

of experimental points, x'_{1i}, x'_{2i} and x'_{1i}(calc), x'_{2i}(calc) are the experimental and calculated mole fractions of one phase, and x''_{1i}, x''_{2i} and x''_{1i}(calc), x''_{2i}(calc) are the experimental and calculated mole fractions of the respective phases. For the NRTL model, the nonrandomness parameter α_{ij} was set at a value of 0.35, 0.40, or 0.45 (see Table 6). The NRTL equation was optimized for all parameters. The parameters $g_{ij} - g_{jj}$ and $g_{ji} - g_{ii}$ are shown in Table 6. The model correlation parameters are included in Table 6, together with the root-mean-square deviation (rmsd) values, defined below, which can be taken as a measure of the precision of the correlation.

$$\mathrm{rmsd} = (\sum_i \sum_l \sum_m [x_{ilm}^{\mathrm{exp}} - x_{ilm}^{\mathrm{calc}}]^2/6k)^{1/2} \qquad (8)$$

where x is the mole fraction and the subscripts i, l, and m designate the component, the phase, and the tie line, respectively, and k is the number of interaction components. Unfortunately the NRTL equation cannot be compared with any other correlation equation, as they were not done.

The effectiveness of the extraction of the alkanol by quinoline is given by its selectivity (*S*), which is the measure of the ability of quinoline to separate an alkanol from water:

$$S = (x_2/x_3)_{\mathrm{quinoline-rich\ phase}}/(x_2/x_3)_{\mathrm{water-rich\ phase}} \qquad (9)$$

where the subscript 2 represents an alkanol and 3 represents water.

This quantity is greater than unity for all the systems reported here, which means that extraction of the alkanol by quinoline is possible. It is, however, not constant over the whole two-phase region. Table 7 lists the maximum *S* values. The order of the selectivity is 1-butanol > 2-butanol > 2-methylpropan-1-ol > 1-propanol > ethanol > methanol, 2-methylpropan-2-ol > 2-propanol.

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Received for review April 7, 1999. Accepted June 30, 1999. The authors wish to thank the FRD (South Africa) and the University of Natal, Durban, for financial support.

JE9900934