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Liquid−Liquid Equilibria for Mixtures of Butanal + an Alkanol + Water at 298.15 K

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Liquid−liquid equilibrium data are presented for mixtures of butanal + an alkanol + water at 298.15 K. The alkanols are methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol. The addition of ethanol or 2-propanol or 2-methyl-2-propanol is found to increase the solubility of water in the butanal more than the others alkanols. The relative mutual solubility of alkanols is higher in the butanal layer than in the water layer. Three three-parameter equations have been fitted to points on the binodal curve. The results are compared and discussed in terms of statistical consistency. 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 better than did the UNIQUAC equation, and the average root mean square deviation phase composition error was 0.003 for the NRTL model and 0.089 for the UNIQUAC model.

Introduction

A great number of industrial seperation processes are concerned with liquid mixtures containing an organic phase and a water phase. This work forms part of a program to determine liquid−liquid equilibria (LLE) for industrially useful mixtures. This work includes LLE and tie-line data of butanal (butyraldehyde) + an alkanol + water mixtures. LLE equilibrium data on systems containing aldehydes are relatively scarce in the literature. Alkanols are being blended with motor fuel and for this reason many workers study ternary mixtures involving an alkanol, water and an organic phase, which is only sparingly soluble in water. In previous studies by Letcher and Sizwana (1992) and Letcher and co-workers (1986, 1989, 1990, 1992, 1993, 1994, 1996) LLE measurements were made on the tertiary mixtures: heptane, *p*-xylene, benzene, toluene, *o*- and -xylene, mesitylene, 1-heptene, 1-heptyne, or diisobutyl ketone + an alkanol + water mixtures at 298.15 K. The alkanols in all the cited publications by Letcher refer to methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol.

In this work the LLE for butanal + an alkanol + water mixtures has been determined for each of the C_1, C_2, C_3, and C_4 alkanols. The data have been compared with mixtures of diisobutyl ketone + an alkanol + water (Letcher *et al*., 1996).

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

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

component	V_{mi}/cm^3·mol^{-1} [a]	n_D exp	n_D lit.[a]	R[b]	Q[b]
butanal	90.54	1.377 0	1.376 6	2.6148	3.2480
methanol	40.70	1.326 58	1.326 52	1.8627	1.9535
ethanol	58.50	1.359 46	1.359 41	2.4952	2.6616
1-propanol	75.20	1.383 68	1.383 70	3.1277	3.3697
2-propanol	76.80	1.374 92	1.375 2	2.9605	3.3433
1-butanol	91.50	1.397 46	1.397 41	3.7602	4.0778
2-butanol	92.00	1.395 32	1.395 30	3.5930	4.0514
2-methyl-1-propanol	92.90	1.393 86	1.393 89	3.7602	4.0922
2-methyl-2-propanol	94.88	1.385 82	1.385 2	3.2195	4.0169
water	18.07	1.332 50	1.332 502 9	1.7334	2.4561

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

Experimental Section

***Chemicals*.** The alkanols were prepared according to the methods given by Furniss *et al*. (1978) and previously discussed by Letcher *et al*. (1992). Methanol, ethanol, and the two propanols were purified and dried by refluxing with magnesium and iodine, followed by distillation. The four butanols were dried by addition of anhydrous potassium carbonate and purified by distillation. Butanal, supplied by Aldrich as 99 mass % reagent, was purified according to the following method. A sample of the aldehyde was mixed with a saturated sodium bicarbonate solution in order to neutralize the *n*-butyric acid in the sample. The butanal phase was then removed, dried repeatedly over calcium chloride, and fractionated in a 20 plate distillation column; the aldehyde was collected as the heart cut of the batch. Freshly purified samples were used in the investigation. The purity of each of the components was determined by GLC and was always better than 99.8 mol %. The physical properties of the reagents used in this work are listed in Table 1 together with literature values.

***Procedure*.** The binodal curves were determined by the titration method described by Letcher and Sizwana (1992). The tie lines were analyzed by two methods which proved

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Table 2. Compositions of Points on the Binodal Curve at 298.15 K for the Systems Butanal (1) + an Alkanol (2) + Water (3), Equilibrium Mole Fraction, x_1, x_2, x_3

x_1	x_2	x_3	x_1	x_2	x_3
Methanol					
0.880	0.000	0.120	0.220	0.279	0.501
0.805	0.046	0.149	0.147	0.264	0.589
0.717	0.109	0.174	0.083	0.228	0.689
0.640	0.160	0.200	0.048	0.175	0.777
0.551	0.204	0.245	0.020	0.100	0.880
0.413	0.253	0.334	0.018	0.045	0.937
0.321	0.277	0.402	0.017	0.016	0.967
0.268	0.282	0.450	0.017	0.000	0.983
Ethanol					
0.880	0.000	0.120	0.209	0.247	0.544
0.804	0.044	0.152	0.195	0.229	0.616
0.735	0.085	0.180	0.103	0.192	0.705
0.645	0.134	0.221	0.084	0.167	0.749
0.500	0.199	0.301	0.061	0.125	0.814
0.406	0.230	0.364	0.029	0.070	0.901
0.322	0.245	0.433	0.019	0.039	0.942
0.270	0.251	0.479	0.017	0.000	0.983
1-Propanol					
0.880	0.000	0.120	0.303	0.286	0.411
0.775	0.070	0.155	0.256	0.295	0.449
0.696	0.119	0.185	0.182	0.300	0.518
0.614	0.165	0.222	0.110	0.279	0.611
0.556	0.194	0.250	0.070	0.250	0.680
0.496	0.220	0.284	0.028	0.147	0.825
0.431	0.247	0.322	0.020	0.065	0.915
0.344	0.277	0.379	0.017	0.000	0.983
2-Propanol					
0.880	0.000	0.120	0.261	0.202	0.537
0.767	0.059	0.174	0.190	0.186	0.624
0.683	0.095	0.222	0.141	0.165	0.694
0.607	0.126	0.267	0.089	0.122	0.789
0.511	0.162	0.327	0.059	0.096	0.845
0.445	0.182	0.373	0.022	0.053	0.925
0.374	0.197	0.429	0.018	0.030	0.952
0.291	0.205	0.504	0.017	0.000	0.983
1-Butanol					
0.880	0.000	0.120	0.272	0.388	0.340
0.825	0.035	0.140	0.229	0.416	0.355
0.739	0.086	0.175	0.164	0.452	0.380
0.695	0.115	0.190	0.124	0.470	0.396
0.644	0.148	0.208	0.050	0.492	0.458
0.569	0.196	0.235	0.030	0.455	0.515
0.523	0.225	0.252	0.019	0.020	0.961
0.434	0.295	0.271	0.018	0.012	0.970
0.380	0.319	0.301	0.017	0.000	0.983
0.336	0.349	0.315			
2-Butanol					
0.880	0.000	0.120	0.261	0.339	0.400
0.812	0.045	0.143	0.180	0.366	0.454
0.735	0.091	0.174	0.091	0.369	0.540
0.639	0.154	0.207	0.050	0.350	0.600
0.552	0.204	0.244	0.030	0.322	0.648
0.497	0.234	0.269	0.020	0.054	0.946
0.430	0.267	0.303	0.018	0.020	0.978
0.340	0.309	0.351	0.017	0.000	0.983
2-Methyl-1-propanol					
0.880	0.000	0.120	0.310	0.390	0.300
0.819	0.045	0.136	0.258	0.427	0.315
0.750	0.085	0.165	0.231	0.445	0.324
0.705	0.116	0.179	0.148	0.493	0.359
0.652	0.154	0.194	0.100	0.519	0.381
0.593	0.193	0.214	0.064	0.532	0.404
0.546	0.226	0.228	0.030	0.548	0.422
0.445	0.297	0.258	0.020	0.021	0.959
0.356	0.359	0.285	0.017	0.000	0.983
2-Methyl-2-propanol					
0.880	0.000	0.120	0.255	0.200	0.545
0.789	0.050	0.161	0.204	0.195	0.601
0.730	0.080	0.190	0.158	0.189	0.653
0.650	0.117	0.233	0.139	0.181	0.680
0.580	0.139	0.281	0.110	0.167	0.723
0.500	0.161	0.339	0.054	0.121	0.825
0.440	0.178	0.382	0.022	0.074	0.904
0.370	0.190	0.440	0.017	0.000	0.983
0.310	0.197	0.493			

Table 3. Compositions of the Conjugate Solutions, x'_1, x'_2 and x''_1, x''_2, at 298.15 K for the Systems Butanal (1) + an Alkanol (2) + Water (3)

water rich		aldehyde rich	
x'_1	x'_2	x''_1	x''_2
	Methanol		
0.016	0.072	0.738	0.094
0.025	0.117	0.652	0.149
0.045	0.167	0.536	0.212
0.060	0.206	0.407	0.255
0.090	0.236	0.278	0.280
	Ethanol		
0.006	0.017	0.783	0.057
0.013	0.035	0.534	0.185
0.027	0.058	0.380	0.236
0.039	0.085	0.234	0.251
0.041	0.092	0.183	0.241
	1-Propanol		
0.004	0.013	0.609	0.166
0.005	0.023	0.449	0.240
0.006	0.035	0.320	0.281
0.008	0.045	0.218	0.299
0.009	0.056	0.151	0.295
0.010	0.067	0.100	0.271
	2-Propanol		
0.008	0.019	0.671	0.100
0.010	0.029	0.550	0.149
0.012	0.035	0.465	0.177
0.018	0.041	0.291	0.204
0.024	0.052	0.197	0.188
	1-Butanol		
0.001	0.003	0.670	0.130
0.001	0.008	0.475	0.256
0.001	0.013	0.326	0.354
0.001	0.016	0.175	0.449
	2-Butanol		
0.001	0.013	0.671	0.134
0.002	0.024	0.468	0.248
0.002	0.035	0.289	0.328
0.001	0.044	0.090	0.370
	2-Methyl-1-propanol		
0.000	0.004	0.664	0.146
0.001	0.009	0.459	0.287
0.001	0.014	0.287	0.408
0.000	0.017	0.180	0.480
	2-Methyl-2-propanol		
0.006	0.019	0.684	0.100
0.010	0.033	0.483	0.168
0.015	0.046	0.249	0.200
0.021	0.062	0.140	0.180

to be consistent. The refractive index method of Briggs and Comings (1943) described by Letcher and Sizwana (1992) was used and supported in one case by a similar technique which involved density measurements. The densities were determined using a high-precision Anton Paar DMA (601) vibrating-tube density meter. 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. The temperature was measured with the accuracy of 0.05 K.

Results

The composition of mixtures on the binodal curve at 298.15 K are given in Table 2 and tie-line compositions are given in Table 3 and are plotted in Figure 1.

Three equations have been fitted to the data following the work of Hlavatý (1972). The coefficients A_i relate to a modified Hlavatý equation:

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

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 a log γ equation

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

where

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

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

and x_1 refers to the mole fraction composition of the butanal, 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 and have been used to summarize the binodal curve data. These equations have been discussed by Letcher *et al.* (1992). The coefficients A_i, B_i, and C_i for $i = 1-3$ for eqs 1−3, respectively, are given in Table 4.

Equations 1−3 have been fitted to the binodal curves with the standard deviations σ. This is defined as

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

where n is the number of data points and 3 is the number of coefficients (Sen and Srivastava, 1990). The standard errors defined by Sen and Srivastava (1990) as the square root of the variance of the estimated coefficients are larger for the modified Hlavatý equation (11% to 500%) than the standard errors for the β function (2% to 9%) and the log γ equations (1% to 6%). The log γ function gave the best fit; i.e. five out of eight result in smaller σ.

Discussion

All the solubility data, summarized in Table 2, in the binary system butanal + water are in good agreement with those obtained by Tapper *et al.* (1985) and the literature cited therein for the butanal and water rich phase. The solubilities of butanal in water are $x_1 = 0.017$ and $x_1 = 0.983$ and the solubilities of water in butanal are $x_3 = 0.870$ and $x_3 = 0.130$, which is comparable with our data shown in Table 2.

The binodal curves in Figure 1a−h show that the solubility of water in butanal + an alkanol is very much dependent on the type of alkanol. In the ternary systems water is most soluble in the systems containing ethanol, 2-propanol, or 2-methyl-2-propanol. Similar results were obtained by Letcher *et al.* (1992) for mixtures of diisopropyl ether or diisobutyl ketone (Letcher *et al.*, 1996) with an alkanol + water. For all alkanols, water is more soluble in butanal than in diisopropyl ether or diisobutyl ketone; i.e. the two-phase region is smaller for the aldehyde mixtures than for the ether or ketone mixtures. For a particular alkanol, water is more soluble in butanal for mixtures containing ethanol than for mixtures containing methanol. For the mixtures containing C_3 alkanols, 2-propanol is a better solvent than 1-propanol and for the mixtures containing C_4 alkanols, water is more soluble in the mixtures containing 2-methyl-2-propanol than the others. Figure 1 shows that the area of the two-phase region for the C_4 alkanol mixtures increases in the order: 2-methyl-2-propanol < 2-butanol < 1-butanol < 2-methyl-1-propanol. The same effect was observed for the diisobutyl ketone mixtures. The shapes of the binodal curves for

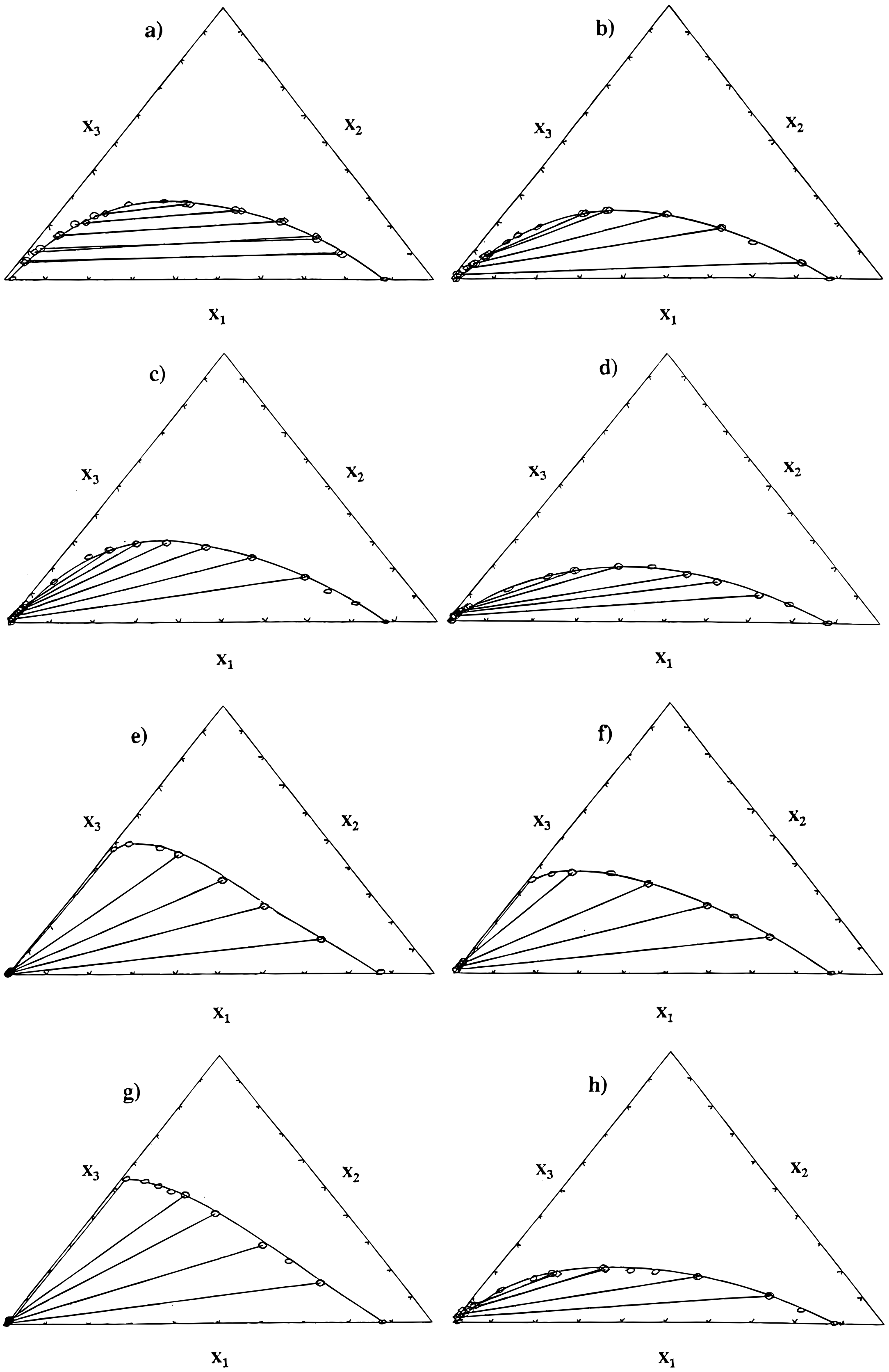

Figure 1. NRTL correlations for the liquid−liquid equilibrium data for the following systems: (a) butanal (1) + methanol (2) + water (3); (b) butanal (1) + ethanol (2) + water (3); (c) butanal (1) + 1-propanol (2) + water (3); (d) butanal (1) + 2-propanol (2) + water (3); (e) butanal (1) + 1-butanol (2) + water (3); (f) butanal (1) + 2-butanol (2) + water (3); (g) butanal (1) + 2-methyl-1-propanol (2) + water (3); (h) butanal (1) + 2-methyl-2-propanol (2) + water (3). Key: (○) experimental points; (◇) predicted points. The solid line is calculated with the log γ equation.

butanal (1) + 1-butanol, 2-butanol, or 2-methyl-1-propanol (2) + water (3) are similar to the shape of the binodal curves for the related diisobutyl ketone mixtures, showing a skewing toward the water axis.

The slope of the tie lines is comparable for all alkanols excluding methanol, which is less soluble in butanal than

Table 4. Coefficients A_i, B_i, and C_i in Eqs 1−3, Respectively, for the Systems Butanal (1) + an Alkanol (2) + Water (3) at 298.15 K[a]

Hlavatý	β	log γ
	Methanol	
$A_1 = -0.12(0.07)$	$B_1 = 1.29(0.06)$	$C_1 = 1.09(0.04)$
$A_2 = 0.12(0.07)$	$B_2 = 1.14(0.02)$	$C_2 = 1.07(0.02)$
$A_3 = 1.14(0.19)$	$B_3 = 1.00(0.02)$	$C_3 = 1.35(0.02)$
$\sigma^b = 0.008$	$\sigma = 0.012$	$\sigma = 0.008$
	Ethanol	
$A_1 = 0.01(0.05)$	$\mathrm{B}_1 = 1.18(0.04)$	$C_1 = 1.02(0.02)$
$A_2 = 0.22(0.06)$	$B_2 = 1.17(0.02)$	$C_2 = 1.11(0.01)$
$A_3 = 1.33(0.15)$	$B_3 = 1.05(0.02)$	$C_3 = 1.44(0.01)$
$\sigma = 0.010$	$\sigma = 0.007$	$\sigma = 0.005$
	1-Propanol	
$A_1 = -0.23(0.10)$	$B_1 = 1.18(0.06)$	$C_1 = 1.04(0.04)$
$A_2 = 0.21(0.10)$	$B_2 = 1.11(0.03)$	$C_2 = 1.06(0.02)$
$A_3 = 1.14(0.27)$	$B_3 = 0.90(0.03)$	$C_3 = 1.28(0.03)$
$\sigma = 0.011$	$\sigma = 0.014$	$\sigma = 0.011$
	2-Propanol	
$A_1 = -0.02(0.04)$	$B_1 = 0.86(0.05)$	$C_1 = 0.73(0.03)$
$A_2 = 0.17(0.05)$	$B_2 = 1.12(0.03)$	$C_2 = 1.05(0.03)$
$= 1.01(0.12)$	$B_3 = 0.98(0.02)$	$C_3 = 1.33(0.03)$
$= 0.006$	$\sigma = 0.005$	$\sigma = 0.005$
	1-Butanol	
$= -1.03(0.34)$	$B_1 = 2.37(0.18)$	$C_1 = 1.89(0.10)$
$= 0.65(0.24)$	$B_2 = 1.46(0.05)$	$C_2 = 1.37(0.03)$
$= 1.16(0.78)$	$B_3 = 1.05(0.03)$	$C_3 = 1.46(0.03)$
$= 0.020$	$\sigma = 0.039$	$\sigma = 0.027$
	2-Butanol	
$= -0.60(0.20)$	$B_1 = 1.84(0.17)$	$C_1 = 1.51(0.09)$
$= 0.40(0.19)$	$B_2 = 1.34(0.06)$	$C_2 = 1.26(0.04)$
$= 1.12(0.54)$	$B_3 = 1.02(0.04)$	$\mathrm{C}_3 = 1.41(0.04)$
$= 0.062$	$\sigma = 0.036$	$\sigma = 0.047$
	2-Methyl-1-propanol	
$= -1.09(0.42)$	$B_1 = 2.59(0.22)$	$C_1 = 2.11(0.13)$
$= 0.70(0.26)$	$B_2 = 1.45(0.05)$	$C_2 = 1.37(0.04)$
$= 1.31(0.93)$	$B_3 = 1.07(0.04)$	$C_3 = 1.49(0.04)$
$= 0.023$	$\sigma = 0.037$	$\sigma = 0.025$
	2-Methyl-2-propanol	
$= -0.26(0.06)$	$B_1 = 0.70(0.03)$	$C_1 = 0.63(0.02)$
$= 0.03(0.06)$	$B_2 = 1.02(0.02)$	$C_2 = 0.98(0.02)$
$= 0.46(0.17)$	$B_3 = 0.80(0.02)$	$C_3 = 1.15(0.03)$
$= 0.006$	$\sigma = 0.005$	$\sigma = 0.003$

The corresponding standard errors are given in parentheses. The standard deviation σ is given by eq 6.

Table 5. Values of the Parameters for the NRTL and UNIQUAC Equations, Determined from Ternary Liquid−Liquid Equilibria for the Systems: Butanal (1) + an Alkanol (2) + Water (3), as Well as the Calculated Root Mean Square Deviation, rms

	parameters (J·mol^{-1})			
	NRTL[a]		UNIQUAC	
component i−j	$g_{ij} - g_{jj}$	$g_{ji} - g_{ii}$	Δu_{ij}	Δu_{ji}
	Methanol			
	(0.012)[b]		(0.075)	
1−2 2−1	−659.51	2434.11	−655.46	2489.52
1−3 3−1	3147.76	9664.96	4321.57	3495.31
2−3 3−2	1071.69	1148.10	−2627.32	8430.73
	Ethanol			
	(0.004)		(0.091)	
1−2 2−1	2787.78	1211.34	−875.33	2448.35
1−3 3−1	3497.46	8972.20	4356.36	3857.16
2−3 3−2	−1345.13	8202.15	−2613.22	8434.81
	1-Propanol			
	(0.001)		(0.070)	
1−2 2−1	−2654.49	8132.60	−492.67	2980.85
1−3 3−1	4401.29	10701.11	4146.29	3865.79
2−3 3−2	−1925.83	9297.72	−1528.16	8385.04
	2-Propanol			
	(0.002)		(0.044)	
1−2 2−1	1761.89	9451.09	−2808.49	2358.69
1−3 3−1	3710.91	9721.23	−4052.86	2518.16
2−3 3−2	−2947.96	13418.13	−667.31	−159.16
	1-Butanol			
	(0.0009)[b]		(0.147)	
1−2 2−1	164.25	20636.22	−2808.07	2358.09
1−3 3−1	5239.75	21922.30	−4095.17	2438.10
2−3 3−2	−957.57	11835.90	−667.30	−159.88
	2-Butanol			
	(0.001)		(0.091)	
1−2 2−1	4502.82	30060.46	109.11	437.12
1−3 3−1	8300.46	40425.66	−3880.18	2437.02
2−3 3−2	−927.25	9938.07	−753.34	−159.70
	2-Methyl-1-propanol			
	(0.0006)		(0.113)	
1−2 2−1	3858.59	39047.85	252.88	46.535
1−3 3−1	12232.00	29846.62	−4025.21	2220.88
2−3 3−2	−1636.38	12267.65	−39.664	−9.6424
	2-Methyl-2-propanol			
	(0.007)		(0.077)	
1−2 2−1	5944.20	15244.01	253.17	417.04
1−3 3−1	3686.84	34672.26	−3372.79	2220.78
2−3 3−2	5310.58	9147.18	1410.53	−172.87

[a] Calculated with $\alpha_{ij} = 0.3$. [b] The rms deviations are given in parentheses.

the other alkanols. In the previous work (Letcher *et al.*, 1992, 1996) the relative mutual solubility of methanol and ethanol was higher in the water layer than in the diisopropyl ether or in the diisobutyl ketone layer.

Tie Lines 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 five ternary systems discussed here. The equations and algorithms used in the calculation of the compositions of liquid phases follows 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

$$F(P) = \sum_{i=1}^{n} [x_{1i}^{\prime\mathrm{exp}} - x_{1i}^{\prime\mathrm{calc}}(PT)]^2 + [s_{2i}^{\prime\mathrm{exp}} - x_{2i}^{\prime\mathrm{calc}}(PT)]^2 + [x_{1i}^{\prime\prime\mathrm{exp}} - x_{1i}^{\prime\prime\mathrm{calc}}(PT)]^2 + [x_{2i}^{\prime\prime\mathrm{calc}}(PT)]^2 7 \quad (7)$$

where P is the set of parameters vector, n is the number of experimental points, $x_{1i}^{\prime\mathrm{exp}}$, $x_{2i}^{\prime\mathrm{exp}}$, and $x_{1i}^{\prime\mathrm{calc}}(PT)$, $x_{2i}^{\prime\mathrm{calc}}(PT)$ are the experimental and calculated mole fractions of one phase, and $x_{1i}^{\prime\prime\mathrm{exp}}$, $x_{2i}^{\prime\prime\mathrm{exp}}$ and $x_{1i}^{\prime\prime\mathrm{calc}}(PT)$, $x_{2i}^{\prime\prime\mathrm{calc}}(PT)$ are the experimental and calculated mole fractions of the respective phases.

The pure component structural parameters R (volume parameter) and Q (surface parameter) in the UNIQUAC equation were obtained from the tables of modified UNIFAC, published by Gmehling *et al.* (1993) (see Table 1).

For the NRTL model, the third nonrandomness parameter, α_{ij}, was set at a value of 0.3, which has given the best results of correlation. The values of the starting parameters for binary systems with butanal were taken from our previous LLE data (Letcher *et al.*, 1996) for related systems. The parameters calculated in this way, $g_{ij} - g_{jj}$, $g_{ji} - g_{ii}$ and Δu_{ij}, Δu_{ji} for the NRTL and UNIQUAC, respectively, are shown in Table 5. A comparison of the experimental and calculated tie lines by NRTL is shown for each system in Figure 1.

The model correlation parameters are included in Table 5, together with the rms values, defined below, which can be taken as a measure of the precision of the correlations:

$$\text{rms} = \left(\sum_i \sum_l \sum_m [x_{ilm}^{\text{exp}}]^2/6k\right)^{1/2} \qquad (8)$$

where x is the mole fraction and the subscripts i, l, and m designate the component, phase, and tie line, respectively. The correlation obtained with the NRTL model is significantly better than that obtained with the UNIQUAC model.

Conclusions

Liquid−liquid equilibrium data for the eight ternary mixtures: butanal (1) + methanol or +ethanol or +1-propanol or +2-propanol or +1-butanol or +2-butanol or +2-methyl-1-propanol or +2-methyl-2-propanol (2) + water (3) were determined at 298.15 K.

The separations of an alkanol from water by extraction with butanal are feasible as can be concluded from the distribution and selectivity data. The three alkanols ethanol, 2-propanol, and 2-methyl-2-propanol are better solvents for the butanal + water mixtures than are the other alkanols at 298.15 K. Three equations have been fitted to binodal curve data.

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

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