Liquid-Liquid Equilibria of Water + Methanol + 1-Octanol and Water + Ethanol + 1-Octanol at Various Temperatures

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We report liquid-liquid equilibrium data and binodal curves for the systems water + methanol + 1-octanol and water + ethanol + 1-octanol at 25, 35, and 45 °C. The data were fitted to the NRTL and UNIQUAC equations.

Introduction

This study is part of a wider program of research on the recovery of light alcohols from dilute aqueous solutions using high molecular weight solvents (*1, 2*). The availability of the relevant liquid-liquid equilibrium (LLE) data is both necessary for the design and simulation of extraction processes and of intrinsic thermodynamic interest. In this paper we report LLE results for the ternary systems water + methanol + 1-octanol and water + ethanol + 1-octanol, for which no such data have previously been published.

Experimental Section

Methanol and ethanol were supplied by Merck with purities >99.7 mass %, and 1-octanol was supplied by Aldrich with a purity >99.2 mass %. These purities were checked periodically during the experiments by chromatography and by measurements of density and refractive index. Water was Milli-Q quality.

Solubility and LLE data were obtianed using cells thermostated to within ±0.02 K that have been described elsewhere (*3*). Equilibrium phase compositions were determined by gas chromatography in a Hewlett-Packard 5890 Series II apparatus that was equipped with a capillary column injector, 25 m × 0.2 mm × 0.3 μm cross-linked HP-FFAP columns, and a TC detector, and was linked to an HP 3396 Series II integration unit. Prior calibration was effected using internal standards in samples prepared by mass on a Mettler AE-240 balance with a precision of ±0.000 01 g. Statistical analysis of the calibration data using Student's and Fisher's tests (*4*) showed the mole fractions determined to be precise to within ±0.0003.

Correlation

The experimental results were correlated with the NRTL and UNIQUAC equations, using the program developed by Sørensen (*5*). The NRTL equations were fitted for each of the three values most widely used for the nonrandomness parameter α, 0.1, 0.2, and 0.3. The values used for the UNIQUAC volume and area parameters (r and q, respectively) are listed in Table 1. For both mixtures, the UNIQUAC equations were fitted using r and q calculated from the group contribution parameters R_k and Q_k published by Magnussen et al. (*6*), and for water + ethanol + 1-octanol the UNIQUAC correlation was also effected using the rather different values of r and q recommended by Prausnitz (*7*). The goodness of fit was calculated in terms of the rms deviation in phase composition

Table 1. Group Volume and Surface Area Parameters

component	r_i	q_i	component	r_i	q_i
1-octanol	6.6219[a]	5.826[a]	methanol	1.431[b]	1.432[b]
ethanol	2.575[a]	2.588[a]	water	0.92[b]	1.40[b]
	2.11[b]	1.972[b]			

[a] From R_k and Q_k (ref 6). [b] From ref 7.

$$F = 100[\sum_k\sum_j\sum_i(x_{ijk} - \hat{x}_{ijk})^2/6M]^{1/2} \qquad (1)$$

and the rms deviation in the solute distribution ratio

$$\Delta\beta = 100[\sum_k|(\beta_k - \hat{\beta}_k)/\beta_k|^2/M]^{1/2} \qquad (2)$$

where M is the number of tie lines, x indicates the experimental mole fraction and $\hat{x}$ the calculated mole fractions, the subscript i indexes components, j phases, and k tie lines, and β_k and $\hat{\beta}_k$ are, respectively, the experimental and calculated solute distribution ratios.

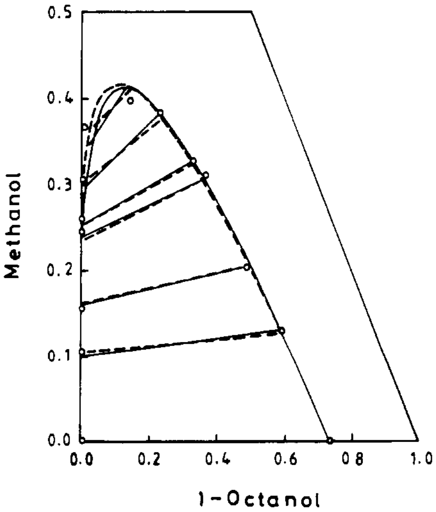

Figure 1. LLE of the system water + methanol + 1-octanol at 25 °C: (○) experimental; (- - -) NRTL correlation; (—) UNIQUAC correlation.

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0021-9568/94/1739-0378$04.50/0

Table 2. LLE Phase Composition as Mole Fractions x for Water (1) + Methanol (2) + 1-Octanol (3)

aqueous phase			organic phase		
x_1	x_2	x_3	x_1	x_2	x_3
T = 298.15 K					
1.0000	0.0000	0.0000	0.2680	0.0000	0.7320
0.8935	0.1056	0.0009	0.2776	0.1314	0.5009
0.8438	0.1556	0.0006	0.3107	0.2043	0.4850
0.7527	0.2461	0.0012	0.3220	0.3110	0.3671
0.7378	0.2606	0.0016	0.3398	0.3289	0.3313
0.6900	0.3066	0.0034	0.3847	0.3840	0.2312
0.6207	0.3676	0.0117	0.4565	0.3995	0.1440
T = 308.15 K					
1.0000	0.0000	0.0000	0.2684	0.0000	0.7376
0.9271	0.0724	0.0006	0.2815	0.0945	0.6240
0.9025	0.0970	0.0005	0.2857	0.1313	0.5831
0.8332	0.1663	0.0005	0.2841	0.2114	0.5045
0.7729	0.2259	0.0012	0.3327	0.2773	0.3900
0.7348	0.2634	0.0019	0.3603	0.3402	0.2995
0.6900	0.3066	0.0034	0.4044	0.3856	0.2100
T = 318.15 K					
1.0000	0.0000	0.0000	0.2581	0.0000	0.7419
0.9451	0.0543	0.0006	0.2710	0.0713	0.6577
0.9097	0.0897	0.0006	0.3885	0.1194	0.5920
0.7826	0.2162	0.0013	0.3557	0.3039	0.3404
0.8205	0.1783	0.0012	0.3126	0.2366	0.4508
0.7506	0.2472	0.0022	0.3755	0.3314	0.2950
0.7001	0.2948	0.0050	0.4314	0.3723	0.1964

Table 3. LLE Phase Compositions as Mole Fractions x for Water (1) + Ethanol (2) + 1-Octanol (3)

aqueous phase			organic phase		
x_1	x_2	x_3	x_1	x_2	x_3
T = 298.15 K					
1.0000	0.0000	0.0000	0.2680	0.0000	0.7320
0.9737	0.0263	0.0000	0.2683	0.0862	0.6275
0.9490	0.0510	0.0000	0.3072	0.1617	0.5311
0.9152	0.0847	0.0001	0.3527	0.2316	0.4157
0.8865	0.1131	0.0004	0.4038	0.2668	0.3094
0.8831	0.1164	0.0005	0.4211	0.2971	0.2819
0.8653	0.1336	0.0011	0.4855	0.3180	0.1965
0.8238	0.1690	0.0072	0.5952	0.2992	0.1056
T = 308.15 K					
1.0000	0.0000	0.0000	0.2684	0.0000	0.7376
0.9789	0.0211	0.0001	0.2915	0.0812	0.6272
0.9563	0.0437	0.0001	0.3120	0.1376	0.5504
0.9288	0.1663	0.0005	0.2841	0.2114	0.5045
0.9101	0.0891	0.0008	0.3927	0.2618	0.3455
0.8795	0.1196	0.0009	0.4722	0.3073	0.2205
0.8580	0.1394	0.0026	0.5231	0.3077	0.1693
T = 318.15 K					
1.0000	0.0000	0.0000	0.2581	0.0000	0.7419
0.9848	0.0152	0.0000	0.3009	0.0643	0.6348
0.9525	0.0474	0.0001	0.3255	0.1679	0.5066
0.9328	0.0669	0.0003	0.3686	0.2170	0.4144
0.9148	0.0849	0.0003	0.3949	0.2606	0.3445
0.8876	0.1115	0.0009	0.4768	0.2952	0.2281
0.8586	0.1389	0.0025	0.5513	0.2984	0.1503

Table 4. Optimized System-Specific Parameters of the NRTL Equation with $\alpha = 0.1$ for the System Water (1) + Methanol (2) + 1-Octanol (3)

i–j	a_{ij} (K)	a_{ji} (K)	i–j	a_{ij} (K)	a_{ji} (K)
T = 298.15 K					
1–2	851.03	–418.70	2–3	399.99	20.68
1–3	4061.00	–748.36			
T = 308.15 K					
1–2	923.50	–417.17	2–3	407.13	90.93
1–3	3847.40	–811.52			
T = 318.15 K					
1–2	7.33	283.58	2–3	404.31	0.56
1–3	3864.80	–825.02			

Results

The experimental results are listed in Tables 2 and 3. The NRTL correlation was best with $\alpha = 0.1$ for water + methanol + 1-octanol, and with $\alpha = 0.2$ for water + ethanol + 1-octanol. The corresponding values of the optimized NRTL binary interaction parameters a_{ij} are listed in Tables 4 and 5, respectively. Table 6 lists the optimized UNIQUAC binary interaction parameters b_{ij} for water + methanol + 1-octanol, Table 7 the values obtained for water + ethanol + 1-octanol using r and q calculated from R_k and Q_k, and Table 8 the values obtained for water + ethanol + 1-octanol using Prausnitz's values (7) of r and q. The goodness-of-fit data listed Table 9 show that both the NRTL and UNIQUAC equations are capable of representing the experimental data well (Figures 1 and 2). In particular both sets of r and q values used for the UNIQUAC correlation of the data for water + ethanol + 1-octanol afforded satisfactory fits.

Table 5. Optimized System-Specific Parameters of the NRTL Equation with $\alpha = 0.2$ for the System Water (1) + Ethanol (2) + 1-Octanol (3)

i–j	a_{ij} (K)	a_{ji} (K)	i–j	a_{ij} (K)	a_{ji} (K)
T = 298.15 K					
1–2	1047.70	–334.67	2–3	325.01	72.98
1–3	1953.58	–64.58			
T = 308.15 K					
1–2	1095.20	–363.32	2–3	292.25	72.79
1–3	2014.4	–65.47			
T = 318.15 K					
1–2	1214.40	–429.57	2–3	345.99	5.33
1–3	2083.90	–72.68			

Table 6. Optimized System-Specific Parameters of the UNIQUAC Equation for the System Water (1) + Methanol (2) + 1-Octanol (3)

i–j	b_{ij} (K)	b_{ji} (K)	i–j	b_{ij} (K)	b_{ji} (K)
T = 298.15 K					
1–2	–334.53	–255.42	2–3	–244.60	28.47
1–3	826.38	61.59			
T = 308.15 K					
1–2	–132.55	–146.52	2–3	–214.52	340.04
1–3	530.08	111.18			
T = 318.15 K					
1–2	–133.47	–229.40	2–3	–268.53	325.79
1–3	583.65	110.06			

Table 7. Optimized System-Specific Parameters of the UNIQUAC Equation ($r_{\text{ethanol}} = 2.575$, $q_{\text{ethanol}} = 2.588$) for the System Water (1) + Ethanol (2) + 1-Octanol (3)

i–j	b_{ij} (K)	b_{ji} (K)	i–j	b_{ij} (K)	b_{ji} (K)
T = 298.15 K					
1–2	215.09	–5.70	2–3	–83.17	273.27
1–3	89.68	327.25			
T = 308.15 K					
1–2	301.74	–70.20	2–3	–116.71	331.97
1–3	132.00	301.92			
T = 318.15 K					
1–2	349.85	–92.69	2–3	–109.45	321.25
1–3	127.89	314.87			

Table 8. Optimized System-Specific Parameters of the UNIQUAC Equation ($r_{\text{ethanol}} = 1.972$, $q_{\text{ethanol}} = 2.11$) for the System Water (1) + Ethanol (2) + 1-Octanol (3)

i–j	b_{ij} (K)	b_{ji} (K)	i–j	b_{ij} (K)	b_{ji} (K)
T = 298.15 K					
1–2	306.54	–78.31	2–3	–54.44	320.58
1–3	56.46	364.99			
T = 308.15 K					
1–2	359.42	–110.15	2–3	–71.43	346.55
1–3	65.82	368.62			
T = 318.15 K					
1–2	362.06	–96.15	2–3	–5.43	256.53
1–3	48.55	398.45			

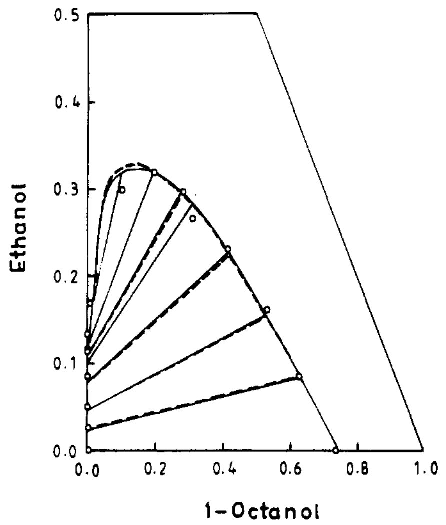

Figure 2. LLE of the system water + ethanol + 1-octanol at 25 °C: (○) experimental; (- - -) NRTL correlation; (—) UNIQUAC correlation.

Conclusions

In both mixtures the concentration of light alcohol is greater in the organic phase than in the aqueous phase. The slope of the tie lines is greater for the mixture with ethanol. The NRTL and UNIQUAC equations are equally satisfactory for correlation if the NRTL parameter α is set to 0.1 for water + methanol + 1-octanol and to 0.2 for water + ethanol + 1-octanol. The two sets of r and q values used for UNIQUAC correlation of the latter system did not afford significantly different results.

Table 9. Values of F $\Delta\beta$ (Eqs 1 and 2) for NRTL and UNIQUAC Equations Fitted to Liquid–Liquid Equilibrium Data

		T = 298.15 K	T = 308.15 K	T = 318.15 K
	Water + Methanol + 1-Octanol			
NRTL (α = 0.1)	$\Delta\beta$	2.3	3.3	3.7
	F	0.7095	0.5684	0.4872
UNIQUAC[a]	$\Delta\beta$	2.7	5.7	3.9
	F	0.6391	0.5868	0.3967
	Water + Ethanol + 1-Octanol			
NRTL (α = 0.2)	$\Delta\beta$	2.2	4.1	2.0
	F	0.4810	0.5405	0.4757
UNIQUAC[b]	$\Delta\beta$	2.5	3.8	3.7
	F	0.5997	0.6193	0.5457
UNIQUAC[a]	$\Delta\beta$	2.3	4.3	2.2
	F	0.5343	0.5658	0.4932

[a] r_i and q_i calculated from R_k and Q_k. [b] r_i and q_i from ref 7.

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Received for review November 3, 1993. Accepted November 30, 1993.® This work was partly supported by the DGICYT (Spain) under Project PB92-0365.

® Abstract published in *Advance ACS Abstracts,* February 1, 1994.