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Liquid−Liquid Equilibria of 1-Octanol + 2-Methoxy-2-methylpropane + Water + Methanol at 25 °C

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We report liquid−liquid equilibrium data for the quaternary system 1-octanol + 2-methoxy-2-methylpropane (MTBE) + water + methanol at 25 °C. Experiments were performed with mixtures with bulk compositions equivalent to systems of the form {water + methanol + [m1-octanol + (1 − m)MTBE]}, where $m = [x_{\text{octanol}}]/[x_{\text{octanol}} + x_{\text{MTBE}}]$ and takes values of 0 (the ternary system water + methanol + MTBE), 0.2, 0.4, 0.6, 0.8, and 1.0 (the ternary system water + methanol + 1-octanol). The quaternary liquid−liquid equilibrium data were correlated by the TK-Wilson, UNIQUAC, and NRTL equations; the UNIQUAC correlation afforded the smallest deviations between experimental and calculated compositions. The quaternary data were satisfactorily predicted by the UNIFAC method.

Introduction

In recent years, the need to optimize industrial processes using solvent extraction has focused attention on equilibria between multicomponent phases. In this work we studied the type 2 (Sørensen and Arlt, 1980) quaternary system {1-octanol + 2-methoxy-2-methylpropane (MTBE) + water + methanol}, which comprises two type 1 ternary subsystems (water + methanol + 1-octanol and water + methanol + MTBE), one type 2 ternary subsystem (water + 1-octanol + MTBE), and one ternary subsystem whose components are miscible in all proportions (methanol + 1-octanol + MTBE). In previous work (Arce et al., 1994a,b, 1996), we obtained equilibrium data for these ternary subsystems at various temperatures (Figure 1b) and correlated these data with the UNIQUAC and NRTL equations, generally obtaining satisfactory results. In the present work we obtained liquid−liquid equilibrium (LLE) data for the quaternary system at 25 °C and correlated these data with Tsuboka and Katayama's (1975) modification of the Wilson (1964) equation, and also with the NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975; Anderson and Prausnitz, 1978) equations. In addition the experimental data were predicted using the UNIFAC method (Fredenslund et al., 1977).

Experimental Section

Materials. MTBE and 1-octanol (both from Aldrich) and methanol (from Merck) had nominal purities >99.8, 99.2, and 99.8 mass %, respectively. These purities were verified by gas chromatography and by measurement of density and refractive index and were checked periodically during the experiments. The water contents of these solvents (measured in a Metrohm 737 KF coulometer) were 0.03 mass % for the methanol and MTBE and 0.02 mass % for the 1-octanol. Water was of Milli-Q quality. The measured densities, refractive indices, and boiling points of these compounds are listed in Table 1, together with values taken from the literature.

Procedure. The quaternary system was studied by taking vertical sections through its tetrahedral composition diagram (Figure 1a), each of these sections corresponding to a pseudoternary system of the form water + methanol + [m1-octanol + (1 −m)MTBE]. The latter component was

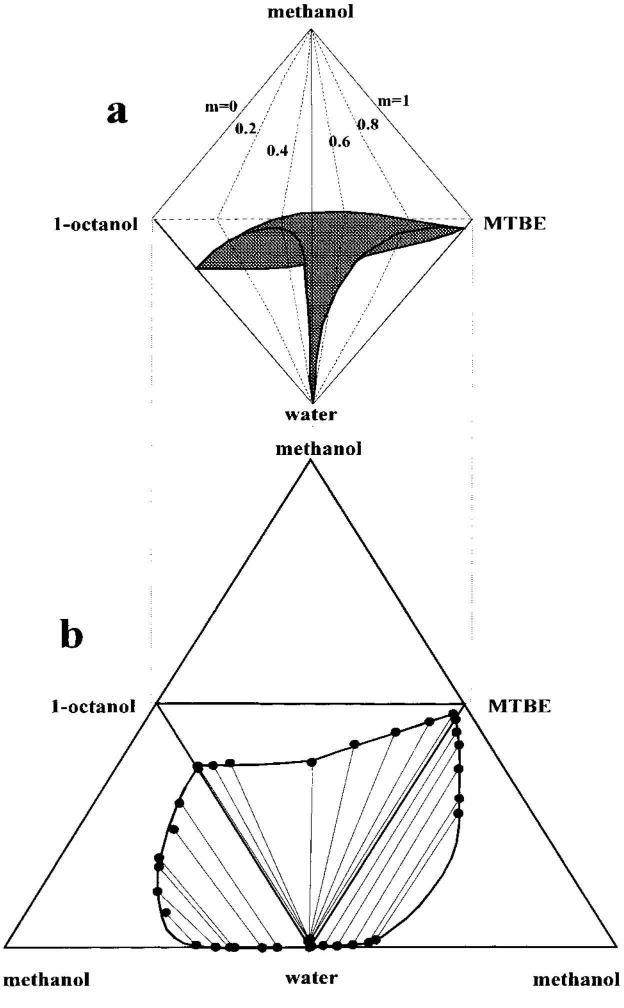

Figure 1. (a) Quaternary two-phase system 1-octanol + 2-methoxy-2-methylpropane + water + methanol at 25 °C. (b) Constituent ternaries for quaternary system.

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Table 1. Densities (d), Refractive Indices (n_D), and Boiling Points (T_b) of the Pure Compounds

	d (298.15 K)/g·cm^{-3}		n_D (298.15 K)		T_b (101.32 kPa)/K	
compound	exptl	lit.	exptl	lit.	exptl	lit
methanol	0.786 6	0.786 64[a]	1.3264	1.326 52[a]	337.75	337.696[a]
1-octanol	0.821 7	0.822 09[a]	1.4275	1.427 50[a]	467.85	468.306[a]
MTBE	0.735 58	0.735 1[b]	1.3663	1.366 3[b]	328.11	328.35[b]
water	0.997 04	0.997 04[a]	1.3324	1.332 50[a]	373.20	373.15[a]

[a] Riddick et al. (1986). [b] Daubert and Danner (1989).

Table 2. Equilibrium Phase Compositions in Mole Fractions (x) for Quaternary Mixtures of 1-Octanol (1) + MTBE (2) + Water (3) + Methanol (4)

organic phase				aqueous phase			
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
	0.9414	0.0586	0.0000		0.0058	0.9942	0.0000
	0.8892	0.0815	0.0293		0.0092	0.9535	0.0373
	0.8373	0.0982	0.0645		0.0083	0.9083	0.0834
	0.7368	0.1503	0.1129		0.0130	0.8542	0.1328
	0.6148	0.2079	0.1773		0.0201	0.7992	0.1807
	0.5544	0.2407	0.2049		0.0306	0.7711	0.1983
0.1549	0.6910	0.1541	0.0000	0.0001	0.0074	0.9925	0.0000
0.1354	0.6319	0.1784	0.0543	0.0001	0.0077	0.9389	0.0534
0.1229	0.5467	0.2186	0.1118	0.0001	0.0153	0.8840	0.1006
0.1292	0.4094	0.2817	0.1797	0.0002	0.0137	0.8340	0.1520
0.0647	0.2756	0.3878	0.2719	0.0011	0.0432	0.7362	0.2195
0.3265	0.4809	0.1926	0.0000	0.0001	0.0024	0.9975	0.0000
0.2829	0.4473	0.2188	0.0509	0.0001	0.0039	0.9571	0.0389
0.2393	0.2793	0.2912	0.1902	0.0002	0.0070	0.8526	0.1402
0.2416	0.2392	0.3052	0.2139	0.0002	0.0083	0.8325	0.1589
0.2084	0.0962	0.3711	0.3243	0.0012	0.0082	0.7511	0.2395
0.5167	0.3038	0.1795	0.0000	0.0003	0.0035	0.9962	0.0000
0.5051	0.2931	0.1857	0.0161	0.0003	0.0041	0.9808	0.0147
0.4582	0.2484	0.2088	0.0846	0.0003	0.0060	0.9123	0.0814
0.4186	0.1913	0.2371	0.1531	0.0004	0.0059	0.8657	0.1280
0.3412	0.1728	0.2746	0.2114	0.0022	0.0082	0.8098	0.1798
0.2825	0.1406	0.3098	0.2671	0.0013	0.0093	0.7625	0.2269
0.1744	0.0716	0.4008	0.3532	0.0079	0.0145	0.6525	0.3251
0.6038	0.1429	0.2533	0.0000	0.0010	0.0011	0.9979	0.0000
0.5526	0.1338	0.2640	0.0496	0.0005	0.0008	0.9618	0.0369
0.4853	0.1070	0.2839	0.1238	0.0002	0.0016	0.9052	0.0931
0.4170	0.0927	0.2947	0.1957	0.0003	0.0017	0.8533	0.1447
0.2880	0.0576	0.3428	0.3116	0.0010	0.0023	0.7495	0.2472
0.7320		0.2680	0.0000	0.0000		1.0000	0.0000
0.5910		0.2776	0.1314	0.0009		0.8935	0.1056
0.4850		0.3107	0.2043	0.0006		0.8438	0.1556
0.3670		0.3220	0.3110	0.0012		0.7527	0.2461
0.3313		0.3398	0.3289	0.0016		0.7378	0.2606
0.2313		0.3847	0.3840	0.0034		0.6900	0.3066
0.1440		0.4565	0.3995	0.0117		0.6207	0.3676
0.0000	0.9463	0.0537		0.0000	0.0109	0.9891	
0.0608	0.8516	0.0876		0.0000	0.0091	0.9909	
0.1506	0.7195	0.1299		0.0000	0.0073	0.9927	
0.2597	0.5603	0.1800		0.0000	0.0055	0.9945	
0.3631	0.3818	0.2551		0.0000	0.0037	0.9963	
0.6297	0.1135	0.2568		0.0000	0.0019	0.9981	
0.6802	0.0525	0.2673		0.0000	0.0001	0.9999	
0.7309	0.0000	0.2691		0.0000	0.0000	1.0000	

a pre-prepared binary mixture of 1-octanol and MTBE for which

$$m = \frac{[x_{\text{octanol}}]}{[x_{\text{octanol}} + x_{\text{MTBE}}]} \tag{1}$$

where x_A is the mole fraction of A in the binary mixture. The precise values of m used were 0, 0.2014, 0.3993, 0.6032, 0.7999, and 1. See Ruiz et al. (1984a,b) for further details of this approach.

Solubility and LLE data for each pseudoternary system were obtained using jacketed cells (Correa et al., 1989) thermostated to within ±0.02 K using a HetoTherm Ultrathermostat. Mixtures were stirred for 2 h and then left to settle for 5 h before samples were withdrawn for analysis. Equilibrium phase compositions were determined by gas chromatography in a Hewlett-Packard 6890 Series apparatus equipped with a capillary column injector, a 25 m × 0.2 mm × 0.3 mm cross-linked HP-FFAP column, and a TC detector linked to an HP 6890 workstation. Calibration used the external standard method. These calibration lines were constructed for each phase. In each case, a series of standard mixtures with compositions lying close to the binodal curve were prepared by weighing (Mettler AE-20 balance, precise to within 0.00001 g) and analyzed by capillary GLC. For the organic phase (rich in MTBE or 1-octanol), the ratio of the mole-fraction compositions for the component pairs water/MTBE, water/1-octanol, and methanol/1-octanol were regressed on the corresponding peak-area ratios. Similarly, for the aqueous phase, the MTBE/water, 1-octanol/water, and methanol/water composition ratios were regressed on the corresponding peak-area ratios. Analysis of a series of samples of known composition indicated that the maximum deviation between the measured and true compositions was ±0.001 mole fraction units. For components present at low concentration (<0.001 mole fraction), the deviation was of the order of 0.0001 mole fraction units.

Results and Data Treatment

Table 2 lists the measured mole-fraction compositions of the aqueous and organic phases of the quaternary system 1-octanol + MTBE + water + methanol at 25 °C. Figure 2 shows two projections of the ends of the tie lines of this system onto a plane parallel to nonintersecting composition axes (Ruiz et al., 1984a,b), the first plane being parallel to the water−MTBE and methanol−1-octanol axes and the second parallel to the water−1-octanol and methanol−MTBE axes. The original plane in which the mixture giving rise to each data point lay is indicated by the value of m cited in the figure.

Correlation. The experimental data were correlated by the TK-Wilson (Tsuboka and Katayama, 1975), UNIQUAC (Abrams and Prausnitz, 1975; Anderson and Prausnitz, 1978), and NRTL (Renon and Prausnitz, 1968) equations using a computer program that minimizes the objective function

$$\text{OF} = \sum_{i=1}^{i=4} (x_{ijk} - \hat{x}_{ijk})^2 \tag{2}$$

where x_{ijk} is the measured composition of component i in phase j on the kth tie line and caps indicate calculated values. In fitting the NRTL equation, the nonrandomness parameter α was set to 0.1, 0.2, or 0.3. For the UNIQUAC correlation, the structural parameters (r and q) of the pure components took the values recommended by Prausnitz et al. (1986) and Magnussen et al. (1981). The resulting binary interaction parameters and root-mean-square (rms) deviations in composition are listed in Table 3.

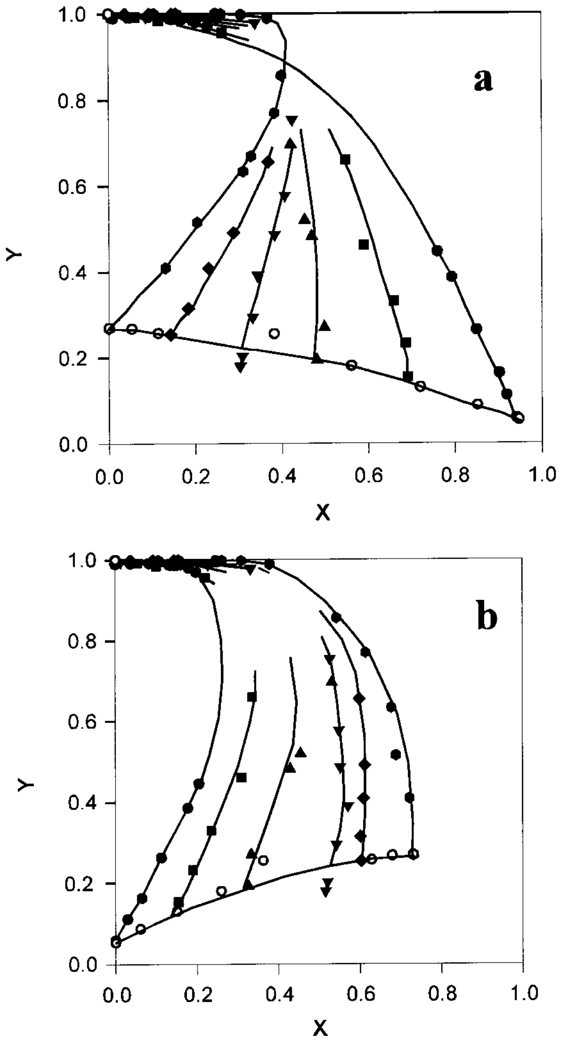

Figure 2. Projection of the ends of the tie lines for the quaternary system onto the plane parallel to (a) the water−MTBE and methanol−1-octanol axes (X = $x_{\text{methanol}} + x_{\text{MTBE}}$ and Y = $x_{\text{methanol}} + x_{\text{water}}$), and (b) the water−1-octanol and methanol−MTBE axes (X = $x_{\text{MTBE}} + x_{\text{1-octanol}}$ and Y = $x_{\text{methanol}} + x_{\text{water}}$): −●− 0.0; −■− 0.2; −▲− 0.4; −▼− 0.6; −◆− 0.8; −⬢− 1.0; −○− base.

Prediction. The experimental LLE data and tie lines were compared with predictions obtained by the UNIFAC method (Fredenslund et al., 1977; Magnussen et al., 1981). The mean deviation between the experimental compositions and the UNIFAC predictions was calculated in terms of the residual *F*

$$F = 100\sqrt{\sum_k \sum_j \sum_i (x_{ijk} - \hat{x}_{ijk})^2/6M} \qquad (3)$$

where *M* is the number of tie lines and the other variables are as defined for eq 2. For the quaternary system the predictions were satisfactory, the mean deviation being 2.13%.

Discussion

Liquid−liquid equilibrium data were determined for the quaternary system 1-octanol + 2-methoxy-2-methylpropane (MTBE) + water + methanol at 25 °C. The use of pseudoternary systems of the form water + methanol + [*m*]-octanol + (1 − *m*)MTBE], each one defined by a vertical plane in the tetrahedral composition diagram for the quaternary system, proved adequate for determination of the solubility curves and for calibration for phase analysis. However, several nonhomogeneous mixtures with compositions lying in one of these vertical planes split into aqueous and organic conjugate phases that had measured compositions slightly outside that plane.

Table 3. Correlation of the LLE Data for the System 1-Octanol (1) + MTBE (2) + Water (3) + Methanol (4): Binary Interaction Parameters (J/mol) and rms Deviation (mole fraction)

model	parameters		rms
UNIQUAC	$\Delta u_{12} = -2620.7$	$\Delta u_{21} = 5292.8$	0.0141
	$\Delta u_{13} = 2066.8$	$\Delta u_{31} = 973.87$	
	$\Delta u_{14} = -3311.3$	$\Delta u_{41} = 5741.7$	
	$\Delta u_{23} = 5077.7$	$\Delta u_{32} = 434.63$	
	$\Delta u_{24} = -3330.8$	$\Delta u_{42} = 4748.4$	
	$\Delta u_{34} = -1633.1$	$\Delta u_{43} = -1233.9$	
TK-Wilson	$\Delta\lambda_{12} = -3026.7$	$\Delta\lambda_{21} = 1619.8$	0.0156
	$\Delta\lambda_{13} = 271.25$	$\Delta\lambda_{31} = 3978.9$	
	$\Delta\lambda_{14} = 5896.5$	$\Delta\lambda_{41} = -2248.0$	
	$\Delta\lambda_{23} = -2947.7$	$\Delta\lambda_{32} = 9354.2$	
	$\Delta\lambda_{24} = 8627.8$	$\Delta\lambda_{42} = -1315.5$	
	$\Delta\lambda_{34} = -2531.0$	$\Delta\lambda_{43} = 242.14$	
NRTL (α = 0.1)	$\Delta g_{12} = -8312.2$	$\Delta g_{21} = 10396$	0.0821
	$\Delta g_{13} = -508.66$	$\Delta g_{31} = 8383.5$	
	$\Delta g_{14} = -4153.6$	$\Delta g_{41} = -4088.2$	
	$\Delta g_{23} = -1418.8$	$\Delta g_{32} = 12467$	
	$\Delta g_{24} = -3530.0$	$\Delta g_{42} = 3402.7$	
	$\Delta g_{34} = -3034.3$	$\Delta g_{43} = 3631.9$	
NRTL (α = 0.2)	$\Delta g_{12} = 6574.6$	$\Delta g_{21} = -7800.7$	0.0403
	$\Delta g_{13} = -40.817$	$\Delta g_{31} = 12413$	
	$\Delta g_{14} = -5582.9$	$\Delta g_{41} = -562.19$	
	$\Delta g_{23} = 2357.2$	$\Delta g_{32} = 7756.8$	
	$\Delta g_{24} = -127.99$	$\Delta g_{42} = 422.70$	
	$\Delta g_{34} = 2549.8$	$\Delta g_{43} = -1843.4$	
NRTL (α = 0.3)	$\Delta g_{12} = 5442.7$	$\Delta g_{21} = -7357.7$	0.0392
	$\Delta g_{13} = 2016.4$	$\Delta g_{31} = 12426$	
	$\Delta g_{14} = -5616.4$	$\Delta g_{41} = 75.012$	
	$\Delta g_{23} = 4075.5$	$\Delta g_{32} = 10610$	
	$\Delta g_{24} = -46.972$	$\Delta g_{42} = -685.17$	
	$\Delta g_{34} = 6048.5$	$\Delta g_{43} = -3830.6$	

The TK-Wilson and UNIQUAC models satisfactorily correlated the experimental data. Compared to these two models, the NRTL equation afforded larger deviations between measured and correlated compositions, at all three values of the nonrandomness parameter tested.

The UNIFAC method satisfactorily predicted the quaternary data, affording a mean deviation that was similar to those obtained for the component ternary subsystems.

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