J. Chem. Eng. Data **1995**, *40*, 1011−1014 **1011**

Isobaric Vapor−Liquid Equilibria of Methanol + 1-Octanol and Ethanol + 1-Octanol Mixtures

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Isobaric vapor−liquid equilibrium data for methanol + 1-octanol and ethanol + 1-octanol have been measured at 101.325 kPa. The results were checked for thermodynamic consistency using Fredenslund *et al.*'s test, correlated using Wilson, NRTL, and UNIQUAC equations for the liquid phase activity coefficients, and compared with the predictions of the ASOG, UNIFAC, and modified UNIFAC group contribution methods.

Introduction

Recovery of solvents used in liquid−liquid extraction is commonly carried out by distillation. In previous papers (Arce *et al.*, 1994, 1995) we have examined recovery by distillation of several solvents used to extract methanol and ethanol from dilute aqueous solutions. In this work we determined vapor−liquid equilibrium (VLE) data at 101.325 kPa for binary mixtures of one such extractant, 1-octanol, with methanol and ethanol. Despite the potential interest in separation of these solvents, we have found no data in the open literature regarding their distillation.

As is usual when VLE data are determined, the thermodynamic consistency of the experimental results was checked using the test of Fredenslund *et al.* (1977b). The results were correlated using the Wilson (Wilson, 1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) equations to calculate the liquid phase activity coefficients, and were compared with the predictions of the group contribution methods ASOG (Kojima and Tochigi, 1979), UNIFAC (Fredenslund *et al.*, 1977a), and modified UNIFAC (Larsen *et al.*, 1987).

Experimental Section

Materials. Methanol and ethanol were supplied by Merck with nominal purities >99.7 and >99.5 mass %, respectively, and 1-octanol was supplied by Aldrich with nominal purity >99.5 mass %; none was subjected to further purification. Table 1 lists the measured densities, refractive indices, and boiling points of the chemicals used, together with published values (Riddick *et al.*, 1986).

Apparatus and Procedure. Distillation was performed in a Labodest apparatus recycling both liquid and vapor phases (Fischer Labor und Verfahrenstechnik, Germany) equipped with a Fischer digital manometer and a Heraeus QuaT100 quartz thermometer that measured to within ±0.01 kPa and ±0.02 K, respectively.

The compositions of vapor and liquid phases were determined by densitometry and refractometry using previously published data for the composition dependence of the densities and refractive indices of the mixtures studied (Arce *et al.*, 1993). Densities were measured to within ±0.000 02 g·cm^{-3} in an Anton Paar DMA 60 digital vibrating tube densimeter equipped with a DMA 602 measuring cell, and refractive indices to within ±0.0001 with an ATAGO RX-1000 refractometer. We estimate the mole fraction compositions derived from these measurements to be precise to within ±0.002.

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

	d(298.15) K/(g·cm−3)		n_D(298.15 K)		T(101.32 kPa)/K	
compound	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]
methanol	0.7866	0.786 64	1.3264	1.326 52	337.75	337.696
ethanol	0.7851	0.785 04	1.3592	1.359 41	351.56	351.443
1-Octanol	0.8217	0.822 09	1.4275	1.427 50	467.85	468.306

[a] Riddick *et al.* (1986).

Table 2. Antoine Coefficients *A*, *B*, and *C* for Eq 2 (Taken from Riddick *et al.* (1986))

compound	*A*	*B*	*C*
methanol	7.205 19	1581.993	239.711
ethanol	7.168 79	1552.601	222.419
1-octanol	5.885 11	1264.322	130.73

Experimental Results and Data Treatment

For vapor and liquid phases in equilibrium at pressure *P* and temperature *T*,

$$y_i\phi_i P = x_i\gamma_i P_i^{s}\phi_i^{s}\exp\left[\frac{V_i^{L}(P-P_i^{s})}{RT}\right] \qquad (1)$$

where x_i and y_i are the mole fractions of component i in the liquid and vapor phases, respectively, γ_i is its activity coefficient, V_i^{L} is its molar volume in the liquid phase, ϕ_i and ϕ_i^{S} are its fugacity coefficients and fugacity at saturation, respectively, and P_i^{S} is its saturated vapor pressure. In this work, V_i^{L} was calculated from the correlation of Yen and Woods (1966), ϕ_i and ϕ_i^{S} were calculated from the second virial coefficient (by the method of Hayden and O'Connell (1975)), and P_i^{S} from Antoine's equation

$$\log(P_i^{s}/\mathrm{kPa}) = A - \frac{B}{t/{}^{\circ}\mathrm{C} + C} \qquad (2)$$

using the coefficients *A*, *B*, and *C* (Table 2) given by Riddick *et al.* (1986).

Fredenslund's test for thermodynamic consistency (Fredenslund *et al.*, 1977b) was applied to the experimental data, yielding a third-order Legendre polynomial for methanol (1) + 1-octanol (2) and a second-order polynomial for ethanol (1) + 1-octanol (2). The mean deviations between the experimental and calculated vapor phase compositions

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0021-9568/95/1740-1011$09.00/0

Table 3. Boiling Temperatures (T), Liquid and Vapor Mole Fractions (x_1 and y_1), Calculated Activity Coefficients (γ_i), and Fugacity Coefficients (ϕ_i) for Methanol (1) + 1-Octanol(2) and Ethanol (1) + 1-Octanol (2) at 101.32 kPa

x_1	y_1	T/K	γ_1	γ_2	ϕ_1	ϕ_2
		Methanol(1) + 1-Octanol(2)				
0.0000	0.0000	467.85		1.0000		0.9622
0.0032	0.1564	461.88	1.3759	1.0000	1.0097	0.9607
0.0079	0.3085	455.06	1.3679	1.0000	1.0042	0.9598
0.0127	0.4072	449.29	1.3601	1.0001	1.0005	0.9598
0.0169	0.5053	444.51	1.3534	1.0002	0.9980	0.9600
0.0242	0.6062	437.95	1.3423	1.0003	0.9952	0.9607
0.0278	0.6674	433.78	1.3371	1.0005	0.9940	0.9607
0.0419	0.7691	424.43	1.3177	1.0010	0.9912	0.9616
0.0592	0.8432	414.68	1.2964	1.0018	0.9890	0.9618
0.1002	0.9109	401.33	1.2557	1.0046	0.9860	0.9612
0.1477	0.9512	388.40	1.2221	1.0084	0.9829	0.9582
0.1635	0.9632	383.64	1.2134	1.0097	0.9816	0.9565
0.2064	0.9756	377.25	1.1949	1.0132	0.9796	0.9542
0.2646	0.9848	368.40	1.1784	1.0175	0.9763	0.9499
0.3662	0.9917	360.18	1.1621	1.0240	0.9726	0.9451
0.4390	0.9937	355.64	1.1525	1.0298	0.9703	0.9420
0.5053	0.9957	352.24	1.1414	1.0388	0.9683	0.9394
0.5823	0.9968	349.62	1.1235	1.0589	0.9667	0.9373
0.6433	0.9973	347.13	1.1051	1.0871	0.9650	0.9351
0.7358	0.9979	344.03	1.0719	1.1647	0.9628	0.9322
0.8143	0.9987	341.99	1.0422	1.2844	0.9613	0.9302
0.8978	0.9990	340.06	1.0152	1.5057	0.9597	0.9282
0.9522	0.9992	338.87	1.0037	1.7360	0.9587	0.9270
0.9819	0.9995	338.15	1.0006	1.9050	0.9581	0.9262
1.0000	1.0000	337.75	1.0000		0.9578	
		Ethanol(1) + 1-Octanol(2)				
0.0000	0.0000	467.85		1.0000		0.9622
0.0044	0.1462	461.91	1.1316	1.0000	1.0044	0.9605
0.0088	0.2612	456.69	1.1309	1.0000	1.0015	0.9593
0.0137	0.3666	452.19	1.1301	1.0000	0.9989	0.9586
0.0210	0.4566	448.10	1.1290	1.0000	0.9962	0.9586
0.0323	0.5599	441.79	1.1272	1.0001	0.9933	0.9586
0.0434	0.6557	435.41	1.1255	1.0001	0.9913	0.9583
0.0579	0.7133	430.80	1.1231	1.0002	0.9898	0.9587
0.0757	0.7840	423.35	1.1202	1.0004	0.9882	0.9581
0.1032	0.8564	413.28	1.1156	1.0008	0.9862	0.9564
0.1494	0.9112	403.52	1.1077	1.0019	0.9842	0.9545
0.2016	0.9473	393.89	1.0985	1.0037	0.9821	0.9514
0.2747	0.9688	384.51	1.0854	1.0074	0.9798	0.9473
0.3619	0.9819	376.14	1.0698	1.0143	0.9775	0.9427
0.4546	0.9880	370.83	1.0539	1.0249	0.9758	0.9393
0.5258	0.9920	367.16	1.0424	1.0358	0.9745	0.9366
0.5697	0.9937	364.98	1.0357	1.0438	0.9737	0.9349
0.6190	0.9948	362.88	1.0288	1.0542	0.9729	0.9332
0.6961	0.9959	360.13	1.0190	1.0737	0.9719	0.9308
0.7840	0.9970	357.31	1.0100	1.1012	0.9707	0.9282
0.8597	0.9981	355.12	1.0044	1.1301	0.9697	0.9260
0.9156	0.9986	353.75	1.0016	1.1550	0.9691	0.9247
0.9492	0.9989	352.85	1.0006	1.1716	0.9686	0.9237
0.9739	0.9992	352.20	1.0002	1.1846	0.9683	0.9230
1.0000	1.0000	351.56	1.0000		0.9680	

(0.0038 for methanol + 1-octanol and 0.0076 for ethanol + 1-octanol) confirm consistency. Table 3 lists the experimental values for x, y, and T together with the activity and fugacity coefficients calculated in the course of applying the Fredenslund test.

Correlation. The experimental (P, T, x, y) results were correlated by a nonlinear regression method based on the maximum-likelihood principle (Anderson *et al.*, 1978). Correlation was performed using the programs published by Prausnitz *et al.* (1980). The models used for the liquid phase activity coefficients were Wilson's equation (Wilson, 1964), the NRTL equation (Renon and Prausnitz, 1968) with the nonrandomness parameter α set to 0.47, and the UNIQUAC equation (Abrams and Prausnitz, 1975) with the area parameter q' set to 0.92 and 0.96 for methanol and ethanol, respectively (Anderson and Prausnitz, 1978) and to 2.71 for 1-octanol. Table 4 lists the model parameters fitted for each system, together with the root mean square deviations in P, T, x, and y. Figures 1 and 2 (for methanol + 1-octanol and ethanol + 1-octanol, respectively) compare the NRTL temperature−composition curves with the corresponding experimental data, and Figures 3 and 4 show, for each of the three models, the differences between the calculated and experimentally measured temperatures of each mixture.

Table 4. Parameters and Root Mean Square Deviations σ of the Wilson, NRTL, and UNIQUAC Activity Models

model	parameters[a]	σ(T)/K	σ(x)	σ(y)	σ(P)/kPa
	Methanol (1) + 1-Octanol (2)				
Wilson	$\Delta\lambda_{12} = 3340.59$, $\Delta\lambda_{21} = -1248.84$	0.17	0.0036	0.0041	0.01
NRTL	$\Delta g_{12} = 3160.42$, $\Delta g_{21} = -970.77$	0.17	0.0032	0.0042	0.01
UNIQUAC	$\Delta u_{12} = 988.01$, $u_{21} = 2555.63$	0.18	0.0042	0.0040	0.01
	Ethanol (1) + 1-Octanol (2)				
Wilson	$\Delta\lambda_{12} = 2387.72$, $\Delta\lambda_{21} = -1312.31$	0.20	0.0029	0.0057	0.02
NRTL	$\Delta g_{12} = 2117.02$, $\Delta g_{21} = -953.57$	0.21	0.0028	0.0057	0.02
UNIQUAC	$\Delta u_{12} = -1005.00$, $\Delta u_{21} = 2668.64$	0.20	0.0031	0.0056	0.02

[a] All energy parameters in J·mol^{-1}.

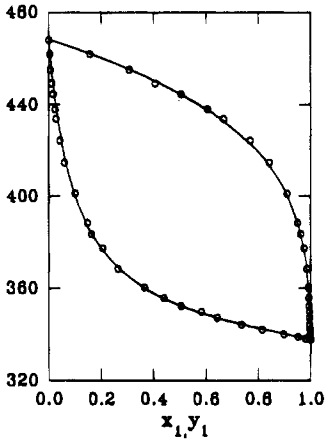

Figure 1. VLE data for methanol (1) + 1-octanol (2) at 101.32 kPa: (○) experimental, (—) NRTL.

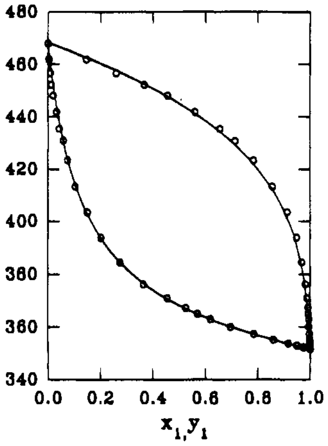

Figure 2. VLE data for ethanol (1) + 1-octanol (2) at 101.32 kPa: (○) experimental, (—) NRTL.

Prediction. The VLE data were predicted using the ASOG (Kojima and Tochigi, 1979), UNIFAC (Fredenslund *et al.*, 1977a) employing the structural and group-interaction parameters recommended by Gmehling *et al.* (1982), and modified UNIFAC (Larsen *et al.*, 1987) group contribu-

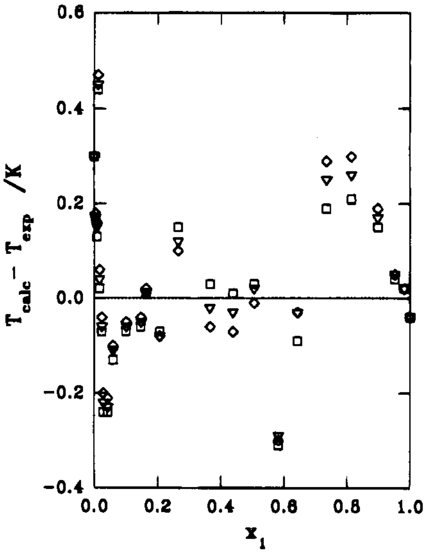

Figure 3. Deviations between the measured temperatures of methanol (1) + 1-octanol (2) mixtures and those calculated using the Wilson (▽), NRTL (□) and UNIQUAC (◇) equations.

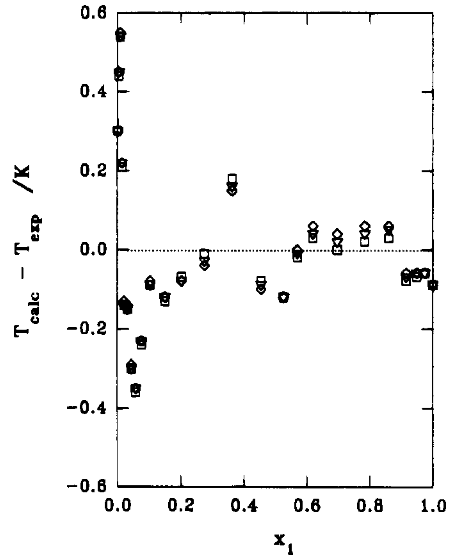

Figure 4. Deviations between the measured temperatures of ethanol (1) + 1-octanol (2) mixtures and those calculated using the Wilson (▽), NRTL (□) and UNIQUAC (◇) equations.

Table 5. Root Mean Square Deviations between the Experimental Temperatures and Vapor Phase Compositions and Those Calculated by the ASOG, UNIFAC and Modified UNIFAC Methods

	ASOG		UNIFAC		modified UNIFAC	
system	σ(T/K)	σ(y)	σ(T/K)	σ(y)	σ(T/K)	σ(y)
methanol (1) + 1-octanol (2)	2.89	0.0381	2.15	0.0278	3.13	0.0184
ethanol (1) + 1-octanol (2)	1.55	0.0240	1.27	0.0147	1.93	0.0281

tion methods to calculate the liquid phase activity coefficients. For the unmodified UNIFAC method, the structural and group interaction parameters recommended by Gmehling *et al.* (1982) were employed. Table 5 lists the root mean square deviations between the experimental VLE data and those predicted by each model. Figures 5 and 6 (for methanol + 1-octanol, and ethanol + 1-octanol, respectively) compare the predicted activity coefficients with those calculated from the experimental data (Table 3).

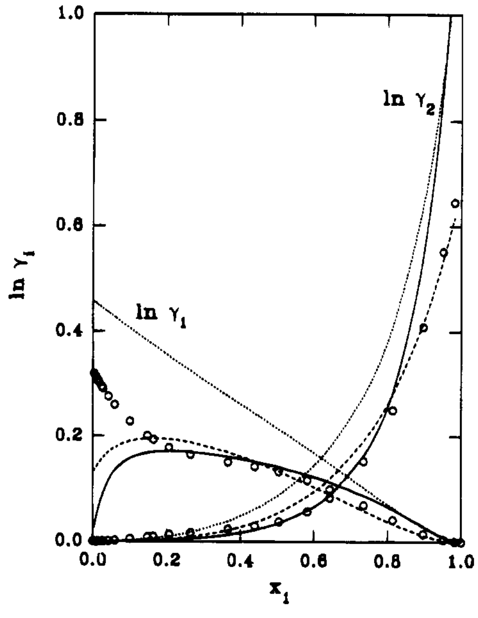

Figure 5. Activity coefficients calculated for methanol (1) + 1-octanol (2) mixtures from the experimental data (○) and by the ASOG (—), UNIFAC (- - -) and modified UNIFAC (···) methods.

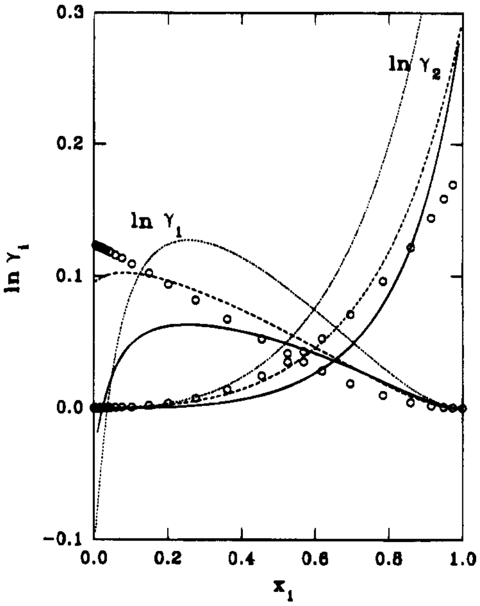

Figure 6. Activity coefficients calculated for ethanol (1) + 1-octanol (2) mixtures from the experimental data (○) and by the ASOG (—), UNIFAC (- - -) and modified UNIFAC (···) methods.

Conclusions

The vapor–liquid equilibrium data reported in this paper for methanol + 1-octanol and ethanol + 1-octanol mixtures at 101.325 kPa are thermodynamically consistent. Both systems exhibit moderate positive deviations from ideal behavior.

The Wilson, NRTL, and UNIQUAC equations for the liquid phase activity coefficients all allow very satisfactory correlation of the experimental temperature–composition results.

Overall, the best predictions of the VLE data were obtained when the UNIFAC method was used to calculate the liquid phase activity coefficient; the modified UNIFAC method gave a slightly better prediction of the vapor phase composition for the methanol + 1-octanol system, although this was at the expense of a poorer prediction of the equilibrium temperature.

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Received for review March 1, 1995. Accepted May 1, 1995.[⊗] This work was partly supported by the DGICYT (Spain) under Project PB92-0365.

JE950052H

[⊗] Abstract published in *Advance ACS Abstracts*, June 15, 1995.