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Isobaric Vapor−Liquid Equilibria of Methanol + Hexyl Acetate and Ethanol + Hexyl Acetate

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Vapor−liquid equilibria of methanol + hexyl acetate and ethanol + hexyl acetate mixtures were determined at 101.32 kPa. The data were checked for thermodynamic consistency using Fredenslund's test, correlated using Wilson, NRTL, and UNIQUAC equations for the liquid phase activity coefficients, and compared with the predictions of the group contribution methods UNIFAC and ASOG.

Introduction

In a previous article (Arce *et al.,* 1993) we examined the possibility of using hexyl acetate for extraction of light alcohols (methanol and ethanol) from aqueous solution. Since alcohol and solvent would generally be separated postextraction by distillation, we have now determined vapor−liquid equilibrium (VLE) data for methanol + hexyl acetate and ethanol + hexyl acetate at 101.32 kPa. As far as we know, no VLE data have previously been published for these systems. The experimental data reported here have been checked for thermodynamic consistency.

The experimental data have also been correlated using Wilson, NRTL, and UNIQUAC equations for the liquid phase activity coefficients and have been compared with the predictions of the group contribution methods UNIFAC and ASOG.

Experimental Section

Chemicals. Water was purified using a Milli-Q Plus system. Methanol and ethanol were supplied by Merck with nominal purities of >99.7 and >99.5 mass %, respectively. Hexyl acetate was supplied by Aldrich with a nominal purity of >99.1 mass %. The purities of all chemicals were confirmed by chromatography; none were subjected to further purification. Table 1 lists the measured densities, refractive indices, and boiling points of the chemicals used, together with recommended values for these properties (Riddick *et al.,* 1986).

Apparatus and Procedure. Distillation was performed with an apparatus recycling both vapor and liquid phases (Labodest, from Fischer Labor und Verfahrenstechnik, Germany). Pressure was measured to a precision of ±0.01 kPa with a Fischer digital manometer, and temperature using a Heraeus QuaT 100 with a precision of ±0.02 K.

The compositions of vapor and liquid phases were determined by densitometry and refractometry using previously published data (Arce *et al.,* 1993, 1994) for the composition dependence of the densities and refractive indices of the mixtures. Densities were measured to within ±0.00001 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. The reported mole fraction compositions are precise to within ±0.002.

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

	d (298.15 K)/g·cm^{-3}		n_D (298.15 K)		T_b (101.32 kPa)/K	
compd	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]
methanol	0.7866	0.78664	1.3264	1.32652	337.75	337.696
ethanol	0.7851	0.78504	1.3592	1.35941	351.56	351.443
hexyl acetate	0.8686	0.8681	1.4069 1.4092[b]	1.4096[b]	444.05	443.7

[a] Riddick *et al.* (1986). [b] At 293.15 K.

Table 2. Antoine Coefficients *A*, *B*, and *C* for Equation 2

compd	A	B	C	ref
methanol	7.20519	1581.993	239.711	Riddick *et al.* (1986)
ethanol	7.16879	1552.601	222.419	Riddick *et al.* (1986)
hexyl acetate	6.46060	1688.630	208.766	see text

Results and Discussion

Experimental Results and Data Reduction. At equilibrium between the vapor and liquid phases at pressure P and temperature T

$$y_i\phi_i P = x_i\gamma_i P_i^s\phi_i^s \exp[V_i^L(P - P_i^s)/RT] \tag{1}$$

where x_i and y_i are the mole fractions of component i in the liquid and vapor phases, respectively, V_i^L is its mole volume in the liquid phase as given by Yen and Woods's correlation (1966), γ_i is its activity coefficient, ϕ_i and ϕ_i^s are its coefficients of fugacity and fugacity at saturation as calculated from the second virial coefficient by Hayden and O'Connell's method (1975) (ϕ_i and ϕ_i^s characterize the deviation of the vapor phase from ideality), and P_i^s is its vapor pressure as calculated from Antoine's equation

$$\log (P_i^s/\text{kPa}) = A - B/(C + T/°C) \tag{2}$$

For methanol and ethanol the parameters A, B, and C were taken from Riddick *et al.* (1986). The values used for hexyl acetate were calculated by a least-squares fit of eq 2 to P_i^s values obtained as follows: P_i^s covering the range 303.15−373.15 K were calculated from eq 2 using Antoine parameters published by Riddick *et al.* (1986); values in the range 373.15−444.05 K were calculated as per Gómez and Thodos (1977, 1978). The standard deviation of the fit was 0.93 Pa. All of the Antoine parameters used are listed in Table 2.

The thermodynamic consistency of the experimental data was checked as per Fredenslund *et al.* (1977b) by fitting second-order Legendre polynomials to the experimental vapor phase compositions. The mean deviations between

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Table 3. Experimental Vapor–Liquid Equilibrium Data and Calculated Activity Coefficients for Methanol (1) + Hexyl Acetate (2) and Ethanol (1) + Hexyl Acetate (2) at 101.32 kPa

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
	Methanol (1) + Hexyl Acetate (2)					Ethanol (1) + Hexyl Acetate (2)			
444.05	0.0000	0.0000		1.0000	444.05	0.0000	0.0000		1.0000
439.45	0.0021	0.0951	1.8115	1.0000	441.51	0.0015	0.0458	2.2917	1.0000
436.19	0.0048	0.1690	1.8140	1.0000	435.95	0.0048	0.1451	2.2799	1.0000
430.55	0.0099	0.2890	1.8186	1.0000	432.75	0.0068	0.2027	2.2728	1.0000
425.93	0.0160	0.3929	1.8236	0.9999	424.75	0.0145	0.3625	2.2457	1.0002
413.26	0.0348	0.5833	1.8370	0.9998	416.96	0.0291	0.5137	2.1956	1.0007
405.01	0.0445	0.6866	1.8426	0.9996	407.69	0.0505	0.6478	2.1253	1.0020
395.41	0.0634	0.7834	1.8510	0.9994	395.80	0.0901	0.7690	2.0044	1.0065
390.10	0.0817	0.8236	1.8559	0.9992	384.05	0.1605	0.8627	1.8156	1.0208
378.29	0.1166	0.8875	1.8571	0.9991	378.98	0.1978	0.8914	1.7276	1.0320
369.86	0.1534	0.9204	1.8474	1.0000	372.78	0.2828	0.9234	1.5542	1.0671
361.47	0.2027	0.9484	1.8187	1.0034	369.55	0.3269	0.9295	1.4773	1.0911
357.32	0.2673	0.9601	1.7588	1.0139	367.58	0.3664	0.9356	1.4151	1.1163
353.43	0.3329	0.9680	1.6790	1.0345	364.10	0.4403	0.9468	1.3140	1.1737
349.49	0.4002	0.9702	1.5848	1.0699	361.62	0.5152	0.9591	1.2293	1.2475
346.81	0.4888	0.9760	1.4538	1.1470	359.36	0.6031	0.9665	1.1499	1.3579
345.10	0.5549	0.9802	1.3582	1.2357	357.87	0.6680	0.9719	1.1034	1.4592
343.44	0.6421	0.9844	1.2425	1.4121	356.69	0.7296	0.9757	1.0679	1.5743
342.42	0.7052	0.9867	1.1697	1.6001	355.56	0.7910	0.9809	1.0403	1.7107
341.14	0.7923	0.9897	1.0879	1.9881	354.54	0.8489	0.9855	1.0210	1.8629
339.65	0.8934	0.9936	1.0245	2.7518	353.37	0.9119	0.9905	1.0071	2.0599
338.79	0.9460	0.9959	1.0065	3.3727	352.09	0.9752	0.9972	1.0006	2.2978
338.15	0.9799	0.9984	1.0009	3.8973	351.56	1.0000	1.0000	1.0000	
337.75	1.0000	1.0000	1.0000						

Table 4. Activity Model Parameters and Root-Mean-Squared Deviations: Wilson, NRTL, and UNIQUAC Models[a]

model	parameters	rms T/K	rms x	rms y	rms P/kPa
	Methanol (1) + Hexyl Acetate (2)				
Wilson	$\Delta\lambda_{12} = 1063.41$, $\Delta\lambda_{21} = 73.73$	0.18	0.0036	0.0037	0.02
NRTL	$\Delta g_{12} = 985.01$, $\Delta g_{21} = 108.05$	0.18	0.0042	0.0038	0.02
UNIQUAC	$\Delta u_{12} = 1957.21$, $\Delta u_{21} = 214.70$	0.18	0.0034	0.0037	0.02
	Ethanol (1) + Hexyl Acetate (2)				
Wilson	$\Delta\lambda_{12} = 920.10$, $\Delta\lambda_{21} = -128.58$	0.51	0.0039	0.0103	0.05
NRTL	$\Delta g_{12} = 596.87$, $\Delta g_{21} = 182.18$	0.51	0.0036	0.0103	0.05
UNIQUAC	$\Delta u_{12} = -446.90$, $\Delta u_{21} = 1312.12$	0.52	0.0044	0.0105	0.05

[a] All energy parameters in cal/mol.

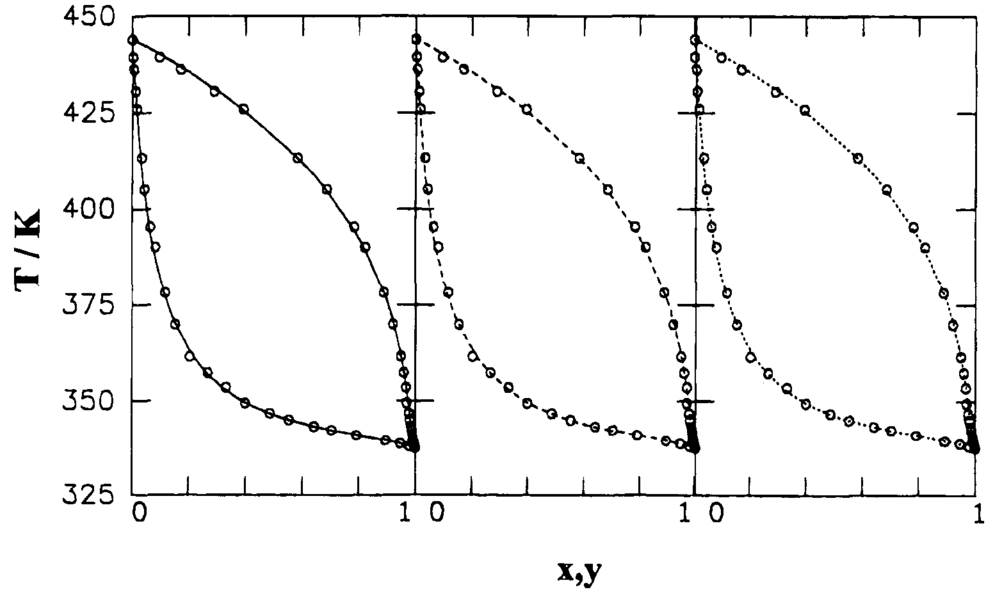

Figure 1. VLE data of the system methanol + hexyl acetate at 101.32 kPa: ○, experimental; —, Wilson; - - -, NRTL ($\alpha = 0.47$); ···, UNIQUAC.

the experimental and calculated values (0.0098 for methanol + hexyl acetate and 0.0099 for ethanol + hexyl acetate) confirm consistency. Table 3 lists the experimental data for x, y, and T together with the activity coefficients calculated in application of the Fredenslund test.

Correlation. The experimental (P, T, x, y) data were correlated by a nonlinear regression method based on the maximum-likelihood principle (Anderson *et al.*, 1978), as implemented in the computer programs published by Prausnitz *et al.* (1980). The models used for the liquid

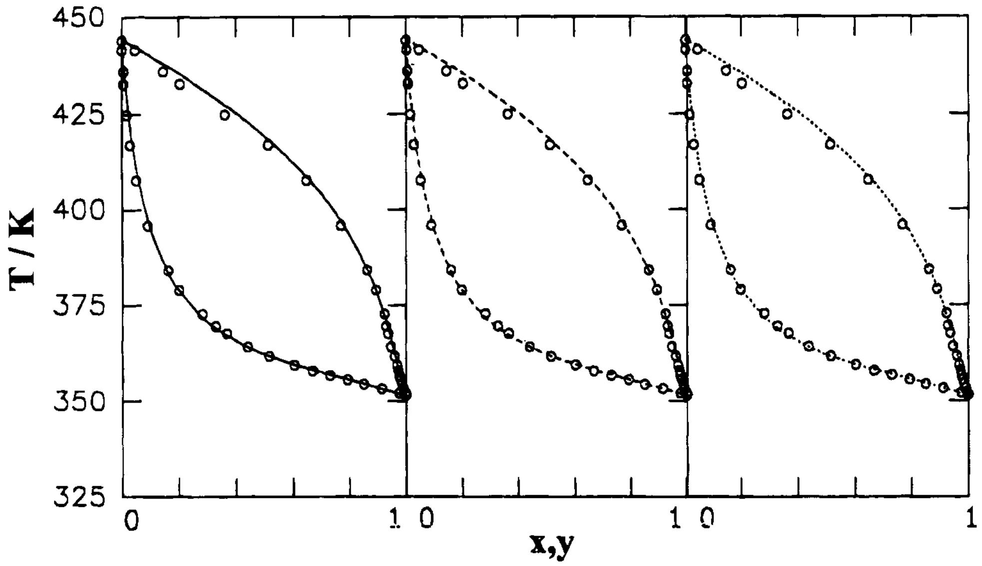

Figure 2. VLE data of the system ethanol + hexyl acetate at 101.32 kPa: ○, experimental; —, Wilson; - - -, NRTL (α = 0.47); ···, UNIQUAC.

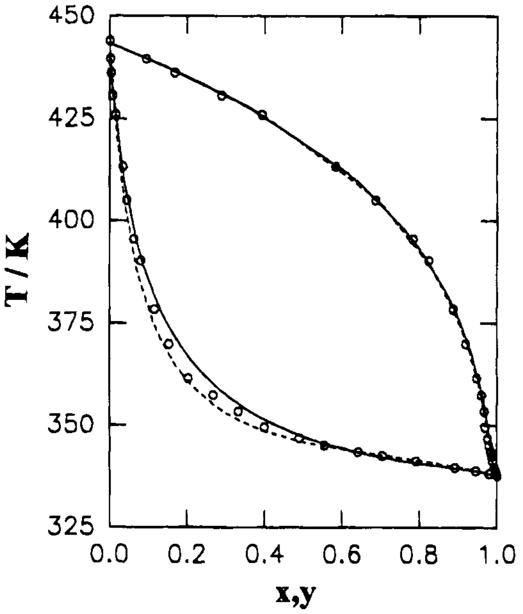

Figure 3. VLE prediction for the system methanol + hexyl acetate at 101.32 kPa: ○, experimental; —, ASOG; - - -, UNIFAC.

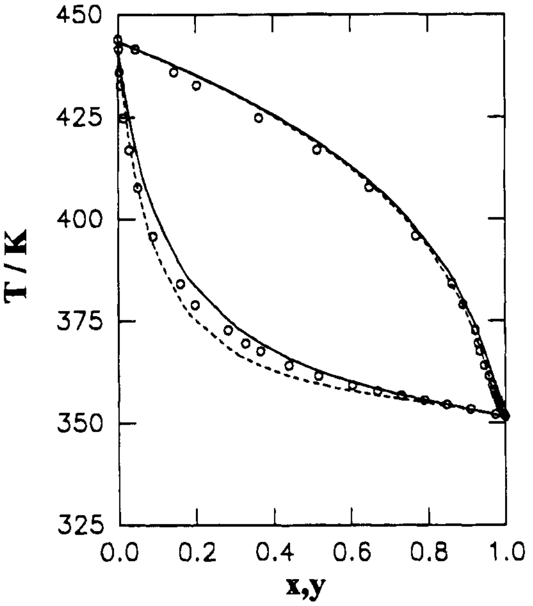

Figure 4. VLE prediction for the system ethanol + hexyl acetate at 101.32 kPa: ○, experimental; —, ASOG; - - -, UNIFAC.

phase activity coefficients were Wilson's equation (1964), the NRTL equation of Renon and Prausnitz (1968) (with the nonrandomness parameter set to 0.47), and the UNIQUAC equation of Abrams and Prausnitz (1975), with the area parameter q' set to 0.92 for methanol and 0.96 for ethanol (Anderson and Prausnitz, 1978). 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 + hexyl acetate and ethanol + hexyl acetate, respectively) compare the temperature–composition curves fitted by each model with the corresponding experimental data.

Prediction. The liquid phase activity coefficients of the mixtures studied were calculated by the group contribution methods ASOG (Kojima and Tochigi, 1979), using the group parameters m_{kl} and n_{kl} originally published by these authors, and UNIFAC (Fredenslund *et al.*, 1977a), using group interaction parameters a_{nm} taken from Gmehling *et al.* (1982). The predicted temperature–composition data are compared with the experimental values in Figures 3 (for methanol + hexyl acetate) and 4 (for ethanol + hexyl acetate). The root-mean-square deviations in T and y are listed in Table 5.

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

	ASOG		UNIFAC	
system	rms T/K	rms y	rms T/K	rms y
methanol + hexyl acetate	1.97	0.0128	2.33	0.0208
ethanol + hexyl acetate	3.88	0.0412	2.51	0.0167

Conclusions. The VLE data reported in this paper for methanol + hexyl acetate and ethanol + hexyl acetate mixtures at 101.32 kPa are thermodynamically consistent. Both systems exhibit strong positive deviation 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 data. Similarly, the ASOG and UNIFAC group contribution methods both afforded satisfactory predictions of the

VLE data, the deviations between experimental and predicted values being small in both cases.

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