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Isobaric Vapor–Liquid Equilibria of Water + Ethanol + Hexyl Acetate

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We determined the isobaric vapor–liquid equilibrium data for the ternary system water + ethanol + hexyl acetate at 101.325 kPa using a distillation apparatus recycling both liquid and vapor phases. The results were compared with those predicted using group contribution methods. The UNIFAC method gave the best predictions.

Introduction

In a previous paper (Arce *et al.*, 1993) we examined the possibility of using hexyl acetate for extraction of ethanol from aqueous solutions. Subsequently, because of the likely use of distillation to recover the extractant, we set about determining the isobaric vapor–liquid equilibrium (VLE) data for this ternary system at 101.325 kPa, in the first instance examining mixtures of ethanol and hexyl acetate (Arce *et al.*, 1995). We now report the VLE data for the ternary system water + ethanol + hexyl acetate. Additionally, the capabilities of the ASOG, UNIFAC, and modified UNIFAC group contribution methods for prediction of the experimental data are compared in this work.

Experimental Section

Materials. Water was purified using a Milli-Q Plus system. Ethanol, supplied by Merck, and hexyl acetate, from Aldrich, had nominal purities of >99.5 and >99.1 mass %, respectively. Neither required further purification. Table 1 lists the measured densities, refractive indices, and boiling points of the chemicals used, together with published values for these parameters (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), which was equipped with a pressure sensor and a Heraeus QuaT100 quartz thermometer that measured to within ±0.01 kPa and ±0.02 K, respectively. Distillation was carried out under an inert atmosphere of argon, which was fed into the still at a constant positive pressure of 101.325 kPa.

The compositions of vapor and liquid phases were determined by densimetry 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 01 g·cm^{-3} in an Anton Paar 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.

Experimental Results and Data Treatment

Results. Isobaric VLE were only determined for the totally miscible mixtures of the three components. Table 2 lists the experimentally determined compositions of the liquid and vapor phases, and the corresponding equilibrium temperatures, and Figure 1 shows the isotherms for the ternary system. The binodal curve shown in Figure 1 is taken from Arce *et al.* (1993), and marks the miscibility limit of the three liquid components at 298.15 K.

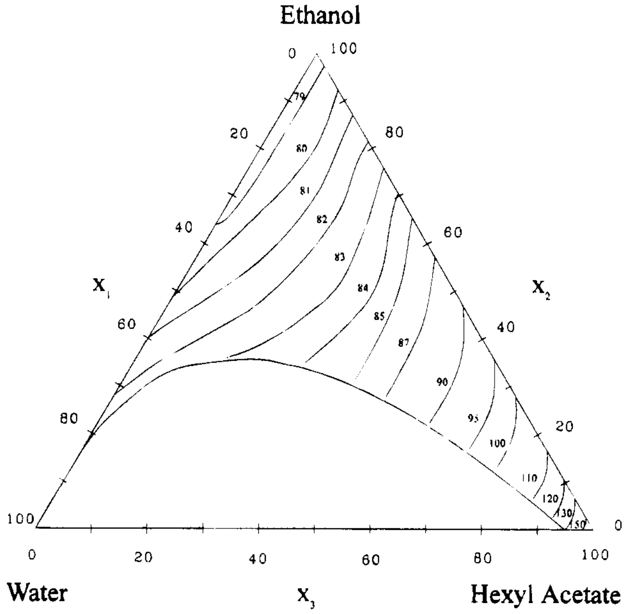

Figure 1. Isotherms for the VLE of the ternary system water (1) + ethanol (2) + hexyl acetate (3) at 101.325 kPa. The binodal curve is from Arce *et al.* (1993), and marks the miscibility limit of the three liquid components at 298.15 K.

The demonstration of the thermodynamic consistency of the experimental VLE for the binary system ethanol + hexyl acetate and the correlation of the *x*, *y*, *P*, and *T* data were detailed in a previous paper (Arce *et al.*, 1995).

Prediction. The computer program used to predict the temperature-composition data is an adaptation of that due to Fredenslund *et al.* (1977b), and considers the nonideal behavior of the vapor and liquid phases in equilibrium, in accordance with the following equation:

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

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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		T_b (101.325 kPa)/K	
compound	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]
water	0.9970	0.997 04	1.3324[b]	1.332 50[b]	373.20	373.15
ethanol	0.7851	0.785 04	1.3592[b]	1.359 41[b]	351.56	351.443
hexyl acetate	0.8686	0.868 1	1.4069[b]		444.05	443.7
			1.4092[c]	1.409 6[c]		

[a] Riddick *et al.* (1986). [b] At 298.15 K. [c] At 293.15 K.

Table 2. Isobaric Vapor–Liquid Equilibrium Data for the System Water (1) + Ethanol (2) + Hexyl Acetate (3): Mole Fractions x_i and y_i of Each Component i in the Liquid and Vapor Phases, Respectively, at Temperature T_b and Pressure 101.325 kPa

x_1	x_2	y_1	y_2	T_b	x_1	x_2	y_1	y_2	T_b
0.1034	0.7917	0.1291	0.8627	353.20	0.0539	0.4997	0.1274	0.8435	360.05
0.0980	0.7519	0.1339	0.8545	353.97	0.0379	0.6147	0.0770	0.8994	357.85
0.0968	0.7091	0.1397	0.8463	354.90	0.0295	0.6962	0.0527	0.9279	356.53
0.0870	0.6423	0.1453	0.8366	356.09	0.0273	0.7530	0.0420	0.9413	355.65
0.0736	0.5701	0.1495	0.8288	357.67	0.0266	0.7927	0.0416	0.9433	354.85
0.1521	0.4934	0.2852	0.6890	357.05	0.0617	0.7811	0.0899	0.8969	354.29
0.2643	0.4053	0.4167	0.5550	356.82	0.0521	0.8176	0.0689	0.9185	353.89
0.3385	0.4105	0.4260	0.5472	356.28	0.0397	0.8534	0.0552	0.9353	353.51
0.4141	0.3785	0.4558	0.5162	356.44	0.0071	0.9777	0.0085	0.9918	351.91
0.5039	0.3707	0.4542	0.5192	356.18	0.0156	0.9435	0.0175	0.9782	352.42
0.5171	0.3894	0.4351	0.5426	355.71	0.0662	0.8980	0.0717	0.9239	352.23
0.5818	0.3439	0.4512	0.5244	355.96	0.3902	0.5856	0.3138	0.6805	352.99
0.6135	0.3252	0.4540	0.5216	356.02	0.4311	0.5370	0.3419	0.6493	353.51
0.6192	0.3751	0.3922	0.6051	354.22	0.4378	0.5111	0.3597	0.6284	353.97
0.5582	0.4374	0.3705	0.6268	353.71	0.4347	0.4944	0.3755	0.6098	354.38
0.5546	0.4283	0.3834	0.6077	354.13	0.2593	0.7342	0.2236	0.7742	351.87
0.5441	0.4116	0.4045	0.5795	354.76	0.2655	0.7108	0.2375	0.7577	352.29
0.5294	0.3954	0.4246	0.5537	355.39	0.2647	0.6895	0.2499	0.7425	352.73
0.1934	0.7881	0.1837	0.8125	351.94	0.2619	0.6763	0.2565	0.7340	353.00
0.1882	0.7699	0.1904	0.8072	352.37	0.2539	0.6641	0.2605	0.7279	353.33
0.1817	0.7334	0.2014	0.7884	353.15	0.2462	0.6582	0.2617	0.7252	353.53
0.1719	0.6941	0.2111	0.7748	353.93	0.3221	0.5834	0.3186	0.6679	353.91
0.1609	0.6470	0.2189	0.7628	354.79	0.2989	0.6052	0.3034	0.6824	353.81
0.1415	0.5918	0.2274	0.7511	355.87	0.2415	0.6543	0.2623	0.7239	353.63
0.1522	0.5949	0.2358	0.7433	355.64	0.2302	0.6338	0.2686	0.7162	354.10
0.1376	0.5432	0.2462	0.7298	356.64	0.2261	0.6135	0.2711	0.7109	354.43
0.1829	0.3864	0.3854	0.5843	358.09	0.2080	0.5909	0.2773	0.7027	354.95
0.2186	0.2955	0.4939	0.4708	358.82	0.1932	0.5638	0.2838	0.6950	355.49
0.1364	0.5681	0.2299	0.7463	356.35	0.1770	0.5166	0.2950	0.6806	356.38
0.2523	0.4758	0.3669	0.6087	356.10	0.0729	0.4425	0.1998	0.7668	360.17
0.0003	0.0025	0.0506	0.0732	438.04	0.1208	0.3693	0.3212	0.6442	359.98
0.0043	0.0242	0.2298	0.3267	417.72	0.2531	0.3750	0.4227	0.5467	357.44
0.0131	0.0384	0.3175	0.3743	407.74	0.2006	0.3572	0.4144	0.5535	358.37
0.0192	0.0561	0.3656	0.4334	396.59	0.1482	0.3368	0.3866	0.5785	359.63
0.0238	0.1036	0.2474	0.6013	387.88	0.1209	0.4452	0.2746	0.6950	358.62
0.0495	0.1697	0.3317	0.5880	374.44	0.0822	0.3433	0.2605	0.6992	362.75
0.0391	0.2206	0.2321	0.6990	371.64	0.0471	0.2660	0.2505	0.6966	367.10
0.0399	0.3003	0.1615	0.7837	368.10	0.3320	0.5549	0.3365	0.6465	354.21
0.0335	0.3975	0.1089	0.8512	364.21	0.3166	0.5239	0.3573	0.6235	354.84
0.0287	0.4598	0.0802	0.8857	362.17	0.0492	0.8401	0.0683	0.9206	353.31

where P and T are the equilibrium pressure and temperature, respectively, x_i and y_i are the mole fractions of component i in the liquid and vapor phases, respectively, V_i^L is its molar volume in the liquid phase, γ_i is its activity coefficient, ϕ_i and ϕ_i^S are its coefficients of fugacity and fugacity at saturation, respectively, and P_i^S is its saturated vapor pressure. In this work, V_i^L was obtained from the correlation of Yen and Woods (1966), γ_i was predicted by the ASOG (Kojima and Tochigi, 1979), UNIFAC (Fredenslund *et al.*, 1977a), or modified UNIFAC (Larsen *et al.*, 1987) group contribution method, ϕ_i and ϕ_i^S were calculated from the second virial coefficient by the method due to Hayden and O'Connell (1975), and P_i^S was calculated from Antoine's equation

$$\log(P_i^S/\text{kPa}) = A - \frac{B}{t/°\text{C} + C} \qquad (2)$$

using the coefficients A, B and C given in Table 3.

Table 3. Antoine Coefficients A, B, and C for Eq 2

compound	A	B	C	ref
water	7.232 55	1750.286	235.000	Hirata *et al.* (1975)
ethanol	7.168 79	1552.601	222.419	Riddick *et al.* (1986)
hexyl acetate	6.460 60	1688.630	208.766	Arce *et al.* (1995)

Table 4. Root Mean Square (rms) Deviations between Experimental and Predicted Values of Temperature T and Mole Fractions y_i of Each Component i in the Vapor Phase for the Water (1) + Ethanol (2) + Hexyl Acetate (3) System at Equilibrium

method	rms (T)/K	rms (y_1)	rms (y_2)	rms (y_3)
ASOG	5.31	0.0270	0.0204	0.0425
UNIFAC	2.08	0.0146	0.0199	0.0109
modified UNIFAC	1.86	0.0206	0.0167	0.0120

Discussion

Table 4 lists the root mean square deviations between the experimentally determined composition and temperature values for the vapor (y and T in eq 1), and those

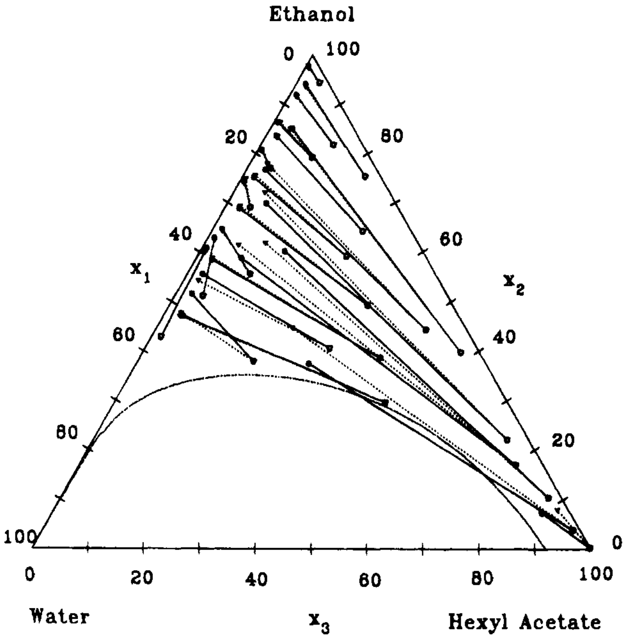

Figure 2. Comparison of the experimental (—, ●) and UNIFAC-predicted (- - -, ▼) VLE data for the ternary system water (1) + ethanol (2) + hexyl acetate (3) at 101.325 kPa.

predicted by each of the three group contribution methods. These deviations show that calculation of the activity coefficient by the UNIFAC and modified UNIFAC methods produced the best predictions, while the ASOG method produced inferior predictions, in particular of the equilibrium temperature.

In Figure 2 the experimental temperature–composition data and those predicted using the UNIFAC method are shown for comparison (the number of points has been reduced for the sake of clarity). The ternary mixture water + ethanol + hexyl acetate did not form an azeotrope.

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