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Vapor−Liquid Equilibria of Propyl Propanoate with 1-Alkanols at 101.32 kPa of Pressure

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The $T-x-y$ measurements for propyl propanoate + ethanol, + 1-propanol, and + 1-butanol obtained at 101.32 kPa in a dynamic ebullometer are reported. All mixtures studied exhibit positive deviations from ideality and are thermodynamically consistent according to the point-to-point test. A minimum boiling azeotrope was found for propyl propanoate (1) + 1-butanol (2) at T = 389.3 K and $x_1 = y_1$ = 0.328. The predictions of the activity coefficients and of the vapor phase compositions show good agreement with the ASOG model and moderate agreement with the UNIFAC model.

Introduction

When the components constituting a mixture are not chemically similar, they are likely to form nonideal solutions, and therefore, their vapor−liquid equilibrium (VLE) behavior cannot be described by Raoult's law. The purpose of the present investigation is to obtain VLE measurements on mixtures of esters and alcohols to provide an insight into the extent of deviation from ideality and to determine if existing semiempirical models can predict the results.

As a continuation of our studies on VLE (Ortega et al., 1986; Ortega et al., 1990; Susial and Ortega, 1993), we present isobaric VLE measurements for propyl propanoate + ethanol, + 1-propanol, and + 1-butanol at 101.32 kPa. Results for propyl propanoate + 1-propanol are compared with literature values (Mozzhukhin, A. S.; Mitropolskaya, V. A.; Serafimov, L. A. *Zh. Fiz. Khim.* **1967**, *41*, 227; see Gmehling et al., 1982). The experimental values are also compared with those estimated by the following group-contribution models: ASOG (Kojima and Tochigi, 1979) and UNIFAC (Fredenslund et al., 1975; Larsen et al., 1986). The latest revisions of these methods (Tochigi et al., 1990; Hansen et al., 1991) do not present modifications in the interaction parameters used for this study.

Experimental Section

Chemicals. All chemicals used in this research were supplied by Fluka AG and were used without further purification. They were degassed simply by ultrasound before use and stored over molecular sieves, type 3 Å, from Fluka. The density, ϱ, refractive index, n, and boiling temperature of the pure substance i, $T_{b,i}$, were measured, and for the 1-alkanols the values obtained did not differ significantly from those published earlier by Galvan et al. (1994). For propyl propanoate (purum >99 mol %) we found the following values: ϱ(298.15 K) = 875.65 kg·m^{-3} (876.7, TRC, 1969), n(D, 298.15 K) = 1.3918 (1.3920, TRC, 1969) and T_b = 395.35 K (395.65, TRC, 1969).

Apparatus and Procedure. Isobaric VLE measurements were made using the dynamic recirculating still described previously (Ortega et al., 1986). Compositions were determined from density using an Anton-Paar having a precision of ±0.02 kg·m^{-3}. Traditionally, the density is correlated as a function of liquid mixture composition using an nth-order polynomial. However, in this work the vapor and liquid samples were obtained through the correlation of the excess volumes versus ester concentration. A more detailed description of the experimental values and correlations used is given in the following section. The accuracies in the mole fraction for the vapor and liquid phases were better than ±0.005 and did not differ significantly from those obtained using the correlations of density vs mole fraction.

Table 1. Densities and Excess Volumes for Propyl Propanoate (1) + 1-Alkanols (2) at 298.15 K

x_1	ϱ/(kg·m^{-3})	10^9V^E/(m^3·mol^{-1})	x_1	ϱ/(kg·m^{-3})	10^9V^E/(m^3·mol^{-1})
Propyl Propanoate (1) + Ethanol (2)					
0.0000	784.96	0	0.3383	832.81	75
0.0945	801.94	25	0.4404	842.16	90
0.1184	805.67	32	0.5354	849.57	99
0.1375	808.52	38	0.6653	858.38	96
0.1737	813.64	44	0.7670	864.24	85
0.2075	818.09	51	0.9061	871.31	48
0.2234	820.07	56	1.0000	875.65	0
0.2799	826.65	67			
Propyl Propanoate (1) + 1-Propanol (2)					
0.0000	799.58	0	0.4988	846.96	112
0.0260	802.80	11	0.5866	852.94	113
0.0634	807.35	25	0.7012	860.00	99
0.2023	822.38	72	0.8096	866.06	72
0.2723	828.84	87	0.8385	867.52	64
0.3477	835.45	102	1.0000	875.65	0
0.4195	841.18	109			
Propyl Propanoate (1) + 1-Butanol (2)					
0.0000	805.98	0	0.5965	852.09	166
0.0870	813.75	52	0.7388	860.85	144
0.1192	816.57	70	0.7526	861.68	138
0.1407	818.46	76	0.8311	866.25	108
0.1777	821.57	94	0.8937	869.76	79
0.2114	824.36	106	0.9460	872.66	47
0.2776	829.61	131	0.9802	874.55	16
0.3481	834.97	149	1.0000	875.65	0
0.4724	843.88	164			
0.5669	850.19	167			

Table 2. Coefficients A_i and k in Eq 1 and Standard Deviations, $s(V^E)$

mixture	k	A_0	A_1	A_2	$10^9s(V^E)$/(m^3·mol^{-1})
propyl propanoate (1)					
+ ethanol (2)	2.718	286	351		1
+ 1-propanol (2)	0.671	434	11	40	1
+ 1-butanol (2)	1.515	656	−117	370	1

Results and Discussion

Densities. For each binary system a set of about 25 mixtures of known composition were prepared by mass

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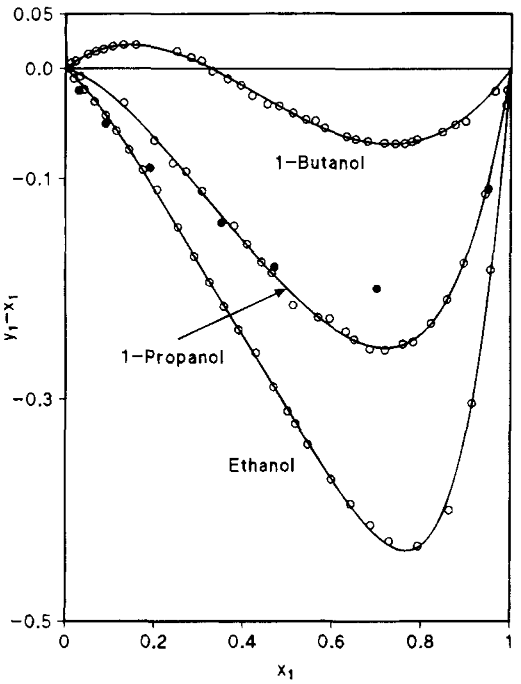

Figure 1. Experimental (○) and calculated values of ($y_1 - x_1$) vs x_1 for the mixtures propyl propanoate (1) + 1-alkanols (2) and (●) experimental points from Gmehling et al. (1982) for propyl propanoate (1) + 1-propanol (2).

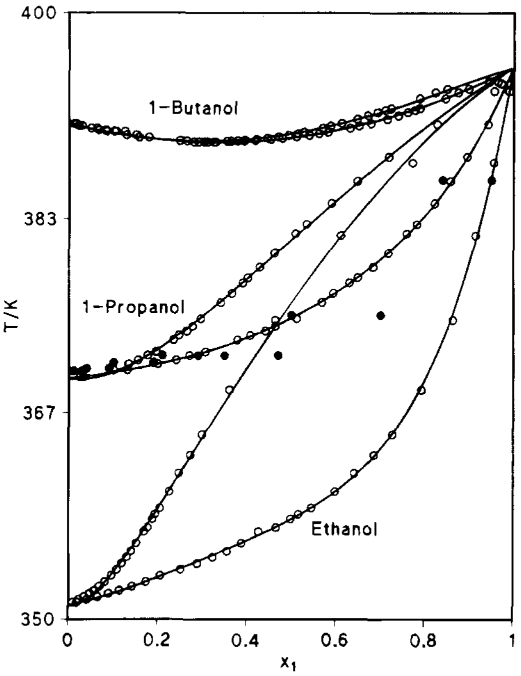

Figure 2. Experimental (○) and calculated values of T vs x_1 or y_1 for the mixtures propyl propanoate (1) + 1-alkanols (2) and (●) experimental points from Gmehling et al. (1982) for propyl propanoate (1) + 1-propanol (2).

Table 3. Experimental Vapor Pressures, $P_i°$, of Propyl Propanoate as a Function of Temperature, T

T/K	$p_i°$/kPa	T/K	$P_i°$/kPa	T/K	$p_i°$/kPa
378.29	61.26	395.79	104.15	402.02	124.29
379.80	64.19	396.47	106.28	402.59	126.33
380.77	66.26	397.08	108.19	403.23	128.53
382.08	69.11	397.78	110.39	403.67	130.11
385.70	77.30	398.38	112.32	404.12	131.71
388.18	83.38	399.03	114.36	404.64	133.67
389.66	87.18	399.72	116.58	405.27	135.95
390.70	89.92	400.39	118.77	405.83	138.12
391.79	92.88	400.92	120.47		
394.27	99.87	401.46	122.28		

using a balance with a resolution of $\pm 10^{-5}$ g. From the density values at 298.15 ± 0.01 K the V^E values were calculated for each ester concentration, and those results are shown in Table 1. The excess volumes were correlated by an equation of the type

$$10^9 V^E/(\mathrm{m^3 \cdot mol^{-1}}) = x_1 x_2 \sum A_i \{x_1/[x_1 + k(1 - x_1)]\} \qquad (1)$$

where x_1 is the ester mole fraction. The coefficients A_i and k, obtained through a least-squares procedure, are given in Table 2. The regular distribution of the points (x_1, V^E) obtained experimentally for each system indicates good values for density; the precision obtained in the vapor, y_i, and liquid, x_i, phase mole fractions was estimated to be ±0.001 unit. No V^E data have been found in the literature for the mixtures studied.

Vapor Pressure. In the thermodynamic treatment of the VLE results the Antoine equation was used to correlate the temperature, T, and vapor pressure $p_i°$, values of the pure liquids. The constants A, B, and C for the 1-alkanols were from other previous works (Ortega et al., 1990; Susial and Ortega, 1993); however, the corresponding values for propyl propanoate, given in Table 4, were obtained by a nonlinear regression with the new vapor pressure results given in Table 3.

Vapor–Liquid Equilibrium Data. Results for propyl propanoate (1) + ethanol (2), + propanol (2), and + butanol (2) at 101.32 ± 0.02 kPa are given in Table 5 along with the activity coefficients, γ_i. Those values were calculated by

$$\ln \gamma_1 = \ln\left(\frac{p y_i}{p_i° x_i}\right) + \frac{(B_{ii} - V_i^L)(p - p_i°)}{RT} + \frac{P}{2RT}\sum_j \sum_k y_j y_k (2\delta_{ji} - \delta_{jk}) \qquad (2)$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \qquad (3)$$

where p is the total pressure and R the universal gases constant. The molar volumes, V_i^L, and the second virial coefficients, B_{ij}, were estimated, respectively, by the modified Rackett equation (see Spencer and Danner, 1972) and the empirical correlations proposed by Tsonopoulos (1974). These same expressions were used in the application of the point-to-point test (Fredenslund et al., 1977) instead of those from Hayden and O'Connell (1975). In this work, the overall deviation of vapor phase composition was less than 0.01 when a third-order expansion was used to

Table 4. Antoine Equation[a] Coefficients, A, B, and C, Used in This Work and Standard Deviation, $s(p_i°)$

	A	B	C	$s(p_i°)$	ref
propyl propanoate	6.011 27	1276.62	76.08	0.06	this work
	6.195 65	1383.66	65.07		Fárková and Wichterle (1993)
ethanol	7.113 02	1513.02	55.15		Ortega et al. (1990)
1-propanol	6.869 85	1434.94	74.98		Ortega et al. (1990)
1-butanol	6.917 01	1572.51	70.04		Susial and Ortega (1993)

[a] Antoine equation: $\log(p_i°/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) - C]$.

Table 5. Vapor–Liquid Equilibrium Data for Propyl Propanoate (1) + 1-Alkanols (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
				Propyl Propanoate (1) + Ethanol (2)					
351.13	0.0000	0.0000		1.000	357.60	0.4667	0.1777	1.233	1.221
351.40	0.0187	0.0097	2.119	0.998	358.31	0.4991	0.1882	1.190	1.252
351.63	0.0417	0.0227	2.203	1.000	358.70	0.5165	0.1942	1.171	1.270
351.86	0.0652	0.0352	2.166	1.004	359.21	0.5458	0.2048	1.147	1.310
352.13	0.0898	0.0473	2.091	1.008	360.57	0.5985	0.2261	1.100	1.376
352.37	0.1141	0.0577	1.989	1.016	362.07	0.6420	0.2476	1.066	1.426
352.71	0.1426	0.0698	1.900	1.023	363.57	0.6866	0.2733	1.044	1.495
353.10	0.1737	0.0816	1.797	1.033	365.25	0.7281	0.3004	1.021	1.569
353.61	0.2060	0.0960	1.748	1.039	368.90	0.7923	0.3604	0.996	1.666
354.10	0.2520	0.1081	1.580	1.069	374.65	0.8628	0.4631	0.975	1.765
354.61	0.2898	0.1192	1.487	1.092	381.58	0.9136	0.6098	0.977	1.654
355.13	0.3243	0.1303	1.424	1.112	387.57	0.9555	0.7725	0.991	1.578
355.63	0.3563	0.1403	1.370	1.134	393.42	0.9900	0.9569	1.004	1.135
356.30	0.3891	0.1520	1.327	1.151	395.65	1.0000	1.0000	1.000	
				Propyl Propanoate (1) + 1-Propanol (2)					
369.83	0.0000	0.0000		1.000	376.88	0.5942	0.3670	1.051	1.228
369.96	0.0329	0.0259	1.693	1.005	377.73	0.6302	0.3914	1.028	1.259
370.53	0.1311	0.1002	1.608	1.013	378.15	0.6488	0.4028	1.014	1.283
371.03	0.1995	0.1344	1.392	1.039	379.03	0.6838	0.4292	0.997	1.323
371.35	0.2411	0.1552	1.315	1.058	380.17	0.7178	0.4622	0.987	1.345
371.75	0.2706	0.1770	1.318	1.058	381.75	0.7579	0.5078	0.979	1.364
372.06	0.3070	0.1957	1.271	1.076	382.53	0.7810	0.5328	0.973	1.396
373.03	0.3783	0.2353	1.200	1.103	384.26	0.8211	0.5896	0.972	1.420
373.40	0.4070	0.2475	1.159	1.124	386.06	0.8577	0.6477	0.969	1.449
373.76	0.4409	0.2651	1.132	1.150	388.05	0.8957	0.7190	0.971	1.483
374.16	0.4637	0.2781	1.114	1.161	390.69	0.9430	0.8284	0.985	1.531
374.78	0.5115	0.2965	1.055	1.217	394.05	0.9920	0.9725	1.000	1.584
376.13	0.5681	0.3421	1.049	1.229	395.65	1.0000	1.0000	1.000	
				Propyl Propanoate (1) + 1-Butanol (2)					
390.85	0.0000	0.0000		1.000	389.67	0.5105	0.4703	1.071	1.104
390.74	0.0116	0.0166	1.645	0.974	389.79	0.5397	0.4936	1.059	1.119
390.60	0.0221	0.0290	1.514	0.976	389.93	0.5615	0.5142	1.055	1.122
390.37	0.0498	0.0629	1.464	0.977	390.05	0.5821	0.5282	1.042	1.139
390.22	0.0670	0.0826	1.434	0.979	390.37	0.6315	0.5698	1.026	1.167
390.12	0.0844	0.1020	1.408	0.980	390.56	0.6521	0.5878	1.019	1.178
390.11	0.1051	0.1253	1.388	0.977	390.78	0.6791	0.6129	1.013	1.192
389.81	0.1290	0.1507	1.370	0.985	391.11	0.7161	0.6483	1.006	1.212
389.63	0.1572	0.1789	1.340	0.990	391.41	0.7410	0.6726	1.000	1.225
389.35	0.2489	0.2647	1.257	1.005	391.69	0.7620	0.6939	0.995	1.236
389.27	0.2804	0.2905	1.226	1.016	391.87	0.7786	0.7123	0.994	1.243
389.27	0.3042	0.3113	1.210	1.020	392.01	0.7894	0.7249	0.994	1.244
389.26	0.3290	0.3265	1.173	1.035	392.83	0.8470	0.7894	0.985	1.279
389.33	0.3646	0.3553	1.148	1.044	393.32	0.8758	0.8246	0.981	1.294
389.35	0.3943	0.3792	1.132	1.055	393.61	0.8994	0.8514	0.978	1.342
389.40	0.4190	0.3946	1.106	1.071	394.19	0.9652	0.9448	0.995	1.421
389.47	0.4529	0.4207	1.088	1.086	395.65	1.0000	1.0000	1.000	
389.56	0.4794	0.4455	1.085	1.090					

represent the results of the three isobaric mixtures; thus, all data sets were shown to be thermodynamically consistent.

The results were analyzed using the dimensionless function g^E/RT as a function of x_1 using the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations and an equation similar to eq 1, previously used by us (Ortega et al., 1986) to correlate VLE data and with the form

$$Q = z(1 - z)\sum A_i\{z/[z + k(1 - z)]\}^i \qquad (4)$$

where z is a variable considered in each case. The coefficients obtained for the above equations and eq 4 are given in Table 6 along the standard deviations. The results indicate that all equations are suitable to represent the data, although the best correlation is given by eq 4. Therefore, this equation was used to fit other equilibrium quantities such as the compositions, x and y, and the temperatures, T, setting $Q_1 = y_1 - x_1$, $Q_2 = T - \sum x_i T_{b,i}$, and $Q_3 = T - \sum y_i T_{b,i}$. Table 7 presents the values for the parameters of eq 4 and $s(Q)$ obtained by correlating the function $y_1 - x_1$ or T vs vapor or liquid phase composition. Figure 1 compares the compositions for the three mixtures considered herein along with the values found in the literature (Mozzhukhin, A. S.; Mitropolskaya, V. A.; Se-

Table 6. Correlation Parameters for Different Equations and Standard Deviations, $s(g^E/RT)$

	Propyl Propanoate (1) + Ethanol (2)		
Margules	$A_{12} = 0.998$	$A_{21} = 0.563$	0.008
Van Laar	$A_{12} = 1.343$	$A_{21} = 1.311$	0.015
Wilson	$A_{12} = 0.347$	$A_{21} = 1.015$	0.009
NRTL ($\alpha = 0.47$)	$\tau_{12} = -0.017$	$\tau_{21} = 1.043$	0.009
UNIQUAC	$\tau_{12} = 0.617$	$\tau_{21} = 1.043$	0.009
eq 4 ($k = 9.39$)	$A_0 = 0.903$	$A_1 = -1.017$	0.003
	Propyl Propanoate (1) + 1-Propanol (2)		
Margules	$A_{12} = 0.758$	$A_{21} = 0.217$	0.006
Van Laar	$A_{12} = 2.642$	$A_{21} = 2.375$	0.016
Wilson	$A_{12} = 0.232$	$A_{21} = 1.564$	0.009
NRTL ($\alpha = 0.47$)	$\tau_{12} = -0.350$	$\tau_{21} = 1.192$	0.009
UNIQUAC	$\tau_{12} = 1.231$	$\tau_{21} = 0.619$	0.009
eq 4 ($k = 3.54$)	$A_0 = 0.657$	$A_1 = -0.686$	0.002
	Propyl Propanoate (1) + 1-Butanol (2)		
Margules	$A_{12} = 0.349$	$A_{21} = 0.268$	0.010
Van Laar	$A_{12} = 2.987$	$A_{21} = 3.089$	0.009
Wilson	$A_{12} = 0.692$	$A_{21} = 1.027$	0.010
NRTL ($\alpha = 0.47$)	$\tau_{12} = -0.049$	$\tau_{21} = 0.394$	0.010
UNIQUAC	$\tau_{12} = 0.838$	$\tau_{21} = 1.069$	0.010

eq 4 ($k = 0.36$) $A_0 = -0.178$ $A_1 = 1.687$ $A_2 = -1.342$ 0.004

Table 7. Coefficients of Eq 4 and Standard Deviation, $s(Q)$, for $Q_1 = y_1 - x_1$ and $z = x_1$, $Q_2 = T - \sum x_i T_{b,i}$ and $z = x_1$, and $Q_3 = T - \sum y_i T_{b,i}$ and $z = y_1$

mixture	function	k	A_0	A_1	A_2	$s(Q)$
propyl propanoate (1) +						
ethanol (2)	Q_1	9.394	0.9030	−1.0166		0.0031
	Q_2	1.46	−36.43	−12.94	−109.60	0.21
	Q_3	0.147	−48.22	68.36		0.33
1-propanol (2)	Q_1	3.542	0.6573	−0.6864		0.0021
	Q_2	3.20	−21.60	−39.63		0.17
	Q_3	0.351	−31.32	35.09		0.22
1-butanol (2)	Q_1	0.359	−0.1781	1.6874	−1.3418	0.0040
	Q_2	0.19	−13.81			0.12
	Q_3	3.98	−14.24	8.72		0.14

rafimov, L. A. *Zh. Fiz. Khim.* **1967**, *41*, 227; see Gmehling et al., 1982) for propyl propanoate + 1-propanol, the corresponding y_1 values show a difference close to 21% which cannot be explained. Figure 2 shows the plots of temperature against composition for the same binary systems; in this case, at the same liquid phase mole fraction, the mean deviation in the temperature was close to 2 K with respect to the above literature values. The azeotrope observed in the mixture propyl propanoate (1) + 1-butanol (2) was determined with the above correlation and setting $y_1 - x_1 = 0$ and $\partial T/\partial x_1 = \partial T/\partial y_1 = 0$ to give an azeotrope at $T = 389.26$ K and $x_1 = y_1 = 0.328$.

The results were also compared with predictions from several group-contribution models. The better estimation of the activity coefficients and of the vapor phase mole fraction was obtained using the ASOG model with an overall mean difference, for the three mixtures, of less than 5%. The predictions with the version of UNIFAC proposed by Larsen et al. (1986) gave an average difference close to 7%, and depending on the interaction pair considered, the version of Fredenslund et al. (1975) with the temperature-independent parameters gave estimations between 11% (CCOH/COOC) and 16% (OH/COOC) in the γ_i values.

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