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Densities and Vapor−Liquid Equilibria in Binary Mixtures Formed by Propyl Methanoate + Ethanol, +Propan-1-ol, and +Butan-1-ol at 160.0 kPa[‡]

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Densities and excess volumes were determined at 298.15 K for propyl methanoate + ethanol, +propan-1-ol, and +butan-1-ol. The results of those quantities were then correlated to get the concentrations of vapor−liquid equilibrium obtained isobarically at 160 kPa for the same mixtures. Two mixtures show azeotropes: for propyl methanoate (1) + ethanol (2), $x_1 = 0.443$ at $T = 358.7$ K; and for propyl methanoate (1) + propan-1-ol (2), $x_1 = 0.762$ at $T = 368.2$ K. The mixtures are thermodynamically consistent, and the predictions made using several group-contribution models are satisfactory.

Introduction

This paper presents isobaric vapor−liquid equilibrium (VLE) values for the binary mixtures formed by propyl methanoate (1) + alkan-1-ol (C_2, C_3, C_4) (2) at 160.0 kPa. Earlier our laboratory published VLE values for these same mixtures at 101.32 kPa (Galván et al., 1994), and those values have been used here, along with the values for the mixture of propyl methanoate (1) + propan-1-ol (2) reported by Mozzhukhim et al. (1967), for purposes of comparison and to examine the evolution of both experimental and theoretical azeotropes in mixtures of methanoate and ethanol or propan-1-ol. To this end, the predictions obtained using various group-contribution methods were considered, as part of an ongoing systematic study of alkanol/ester interactions. As in the past, the ASOG model (Tochigi et al., 1990), the original UNIFAC model as proposed by Fredenslund et al. (1975), and a modified version recently put forward by the Dortmund group (Gmehling et al., 1993) were employed, inasmuch as the version of the UNIFAC model proposed by Larsen et al. (1987) does not contemplate the OH/HCOO interaction specific to methanoate.

Experimental Section

Components. All the components employed in the experiments were of the highest commercial grade. The propyl methanoate was from Aldrich (+99 mol %) and the alkan-1-ols were from Fluka (>99.5 mol %). Prior to use all components were degassed using ultrasound and then dried on a molecular sieve (0.3 nm, from Fluka). The values of the most important physical properties for the pure components *i*, namely, density, ρ, and the refractive index, $n(D,T)$, measured at 298.15 K, and the normal boiling temperature, $T^{o}_{b,i}$, were virtually the same as the values published previously by Galván et al. (1994).

Equipment and Procedure. The ebulliometer used in this study was a small-capacity equilibrium still (approximately 60 cm^3) in which both phases were refluxed. A detailed description of the basic equipment and associated apparatus for taking pressure and temperature measurements has been published elsewhere by Ortega and Susial (1991).

Table 1. Densities and Excess Volumes for Propyl Methanoate (1) + Alkan-1-ols (2) at 298.15 K

x_1	ρ/kg·m^{-3}	$10^9\ V^E_m$/ m^3·mol^{-1}	x_1	ρ/kg·m^{-3}	$10^9\ V^E_m$/ m^3·mol^{-1}
Propyl Methanoate (1) + Ethanol (2)					
0.0000	784.94	0	0.5699	862.96	73
0.0584	795.51	16	0.7131	876.47	65
0.1300	807.42	31	0.8179	885.36	52
0.1914	816.86	42	0.9077	892.44	34
0.3144	833.88	59	0.9540	895.93	19
0.4041	844.94	67	1.0000	899.22	0
0.5124	857.02	73			
Propyl Methanoate (1) + Propan-1-ol (2)					
0.0000	799.54	0	0.5032	854.65	166
0.0104	800.85	8	0.5702	861.14	162
0.0435	804.89	27	0.6104	864.96	157
0.0598	806.82	38	0.6956	872.85	139
0.1026	811.87	62	0.7785	880.30	113
0.1669	819.26	93	0.9073	891.40	62
0.2108	824.19	111	0.9355	893.85	39
0.2323	826.50	124	0.9598	895.88	26
0.3127	835.23	144	0.9800	897.59	11
0.3674	840.98	153	1.0000	899.22	0
0.4025	844.56	161			
Propyl Methanoate (1) + Butan-1-ol (2)					
0.0000	805.93	0	0.5704	858.55	212
0.0156	807.11	13	0.6016	861.49	207
0.0536	810.52	53	0.6375	864.82	202
0.0751	812.54	66	0.7466	875.12	164
0.1252	817.15	102	0.7772	878.05	145
0.1991	823.98	143	0.8326	883.23	124
0.2385	827.55	172	0.9183	891.39	67
0.2648	830.01	180	0.9331	892.76	60
0.3588	838.76	207	0.9514	894.59	38
0.4502	847.26	221	0.9828	897.56	16
0.5264	854.38	221	1.0000	899.22	0

Table 2. Coefficients V_i and $k_v = V^o_2/V^o_1$ in Eq 1 and Standard Deviations $\varsigma(V^E_m)$

mixture	$10^6V^o_i$/ m^3·mol^{-1}	k_v	V_0	V_1	V_2	$10^9\varsigma(V^E_m)$/ m^3·mol^{-1}
propyl methanoate (1)	97.98[a]					
+ethanol (2)	58.69[a]	0.599	323	−273	345	2
+propan-1-ol (2)	75.16[a]	0.767	676	−21		2
+butan-1-ol (2)	91.97[a]	0.939	945	−109		3

[a] Experimental values from Table 1.

The composition of the liquid and vapor phase were determined indirectly from the density values obtained using an Anton Paar model DMA-55 densimeter thermostated to (298.15 ± 0.01) K to a precision of ±0.02 kg·m^{-3}. The compositions of the phases were calculated using simple polynomial correlations for density−ester concen-

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[†] Deceased.

[‡] This paper is dedicated to the memory of J. Falcón, who was unable to witness the conclusion of this research project.

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Table 3. Coefficients, *a*, *b*, *c*, and *d*, and Standard Deviations, $\varsigma(p_i^o)$, in kPa obtained for the Wagner Equation and Comparison with Literature

compound	a	b	c	*d*	*T*/K	$\varsigma(p_i^o)$
propyl methanoate	−4.1171	−6.7749	10.5296	−45.3952	335−365[a]	0.07
ethanol	−8.5980	0.7637	−6.9920	14.4835	340−360[b]	0.02
	−8.6094	0.6148	−6.5951	14.6470	332−512[d]	
propan-1-ol	−7.4983	−0.9672	−8.0657	30.9005	360−377[b]	0.03
	−8.3286	0.8324	−9.8186	22.1611	351−526[d]	
butan-1-ol	−7.4295	−0.5204	−9.5439	33.0060	360−405[c]	0.08
	−6.4683	−3.3290	−2.4942	−11.5661	293−399[d]	

[a] Experimental data taken from Galván et al. (1994). [b] From Ortega et al. (1990). [c] From Susial and Ortega (1993). [d] Smith and Srivastava (1986).

Table 4. Vapor−Liquid Equilibrium Data for Propyl Methanoate (1) + Alkan-1-ols (2) at 160.0 kPa

T/K	x_1	y_1	γ_1	γ_2	*T*/K	x_1	y_1	γ_1	γ_2
Propyl Methanoate (1) + Ethanol (2)									
363.00	0.0000	0.0000		1.000	358.83	0.4729	0.4581	1.263	1.208
362.65	0.0258	0.0485	2.198	1.002	358.84	0.5025	0.4745	1.231	1.240
362.21	0.0376	0.0704	2.217	1.006	359.18	0.6110	0.5281	1.116	1.407
361.41	0.0633	0.1105	2.114	1.017	359.60	0.6618	0.5544	1.068	1.505
360.64	0.1019	0.1640	1.992	1.025	360.06	0.7029	0.5801	1.039	1.589
360.31	0.1271	0.1950	1.917	1.027	360.88	0.7417	0.6102	1.011	1.648
359.84	0.1673	0.2383	1.804	1.036	361.22	0.7716	0.6356	1.003	1.721
359.73	0.1967	0.2667	1.723	1.038	361.98	0.8125	0.6774	0.993	1.807
359.34	0.2431	0.3093	1.635	1.052	363.35	0.8633	0.7445	0.988	1.871
359.15	0.2740	0.3341	1.576	1.065	364.05	0.8895	0.7833	0.989	1.916
359.08	0.2935	0.3488	1.539	1.073	365.14	0.9231	0.8340	0.985	2.032
359.01	0.3231	0.3719	1.493	1.083	366.02	0.9449	0.8722	0.982	2.118
358.88	0.3569	0.3929	1.434	1.107	366.95	0.9665	0.9174	0.984	2.182
358.80	0.3793	0.4074	1.402	1.123	367.60	0.9804	0.9489	0.986	2.257
358.76	0.4266	0.4342	1.330	1.162	368.46	1.0000	1.0000	1.000	
Propyl Methanoate (1) + Propan-1-ol (2)									
382.37	0.0000	0.0000		1.000	370.18	0.4828	0.6016	1.184	1.185
380.97	0.0228	0.0653	2.064	1.008	369.87	0.5128	0.6211	1.160	1.210
380.09	0.0464	0.1168	1.854	1.005	369.59	0.5431	0.6404	1.138	1.237
379.65	0.0594	0.1436	1.800	1.003	369.27	0.5741	0.6572	1.115	1.280
378.51	0.0877	0.1968	1.719	1.009	369.00	0.6018	0.6748	1.100	1.312
378.03	0.1034	0.2239	1.679	1.008	368.76	0.6287	0.6919	1.086	1.344
377.23	0.1246	0.2543	1.615	1.020	368.60	0.6604	0.7090	1.064	1.397
376.79	0.1453	0.2814	1.549	1.022	368.56	0.6980	0.7275	1.034	1.473
376.61	0.1535	0.2919	1.528	1.023	368.46	0.7327	0.7486	1.017	1.541
375.87	0.1834	0.3253	1.453	1.037	368.25	0.7807	0.7688	0.985	1.741
374.96	0.2179	0.3649	1.404	1.052	368.27	0.8177	0.7933	0.970	1.871
374.39	0.2421	0.3925	1.379	1.060	368.31	0.8828	0.8540	0.966	2.054
373.81	0.2701	0.4204	1.344	1.072	368.37	0.9172	0.8890	0.967	2.206
373.29	0.2912	0.4426	1.331	1.081	368.40	0.9440	0.9234	0.975	2.249
372.87	0.3086	0.4610	1.322	1.088	368.42	0.9674	0.9551	0.980	2.254
372.09	0.3500	0.4986	1.287	1.107	368.44	0.9830	0.9769	0.985	2.220
370.87	0.4297	0.5629	1.222	1.149	368.46	1.0000	1.0000	1.000	
Propyl Methanoate (1) + Butan-1-ol (2)									
403.63	0.0000	0.0000		1.000	385.17	0.3519	0.6266	1.155	1.063
401.85	0.0221	0.0846	1.702	0.992	383.99	0.3870	0.6589	1.137	1.070
400.23	0.0429	0.1485	1.594	0.992	382.94	0.4181	0.6848	1.122	1.081
398.63	0.0610	0.1981	1.548	1.002	381.55	0.4584	0.7178	1.110	1.093
396.59	0.0998	0.2835	1.416	0.998	380.66	0.4897	0.7390	1.093	1.108
393.01	0.1653	0.3978	1.300	1.017	379.07	0.5482	0.7743	1.065	1.147
391.79	0.1929	0.4382	1.262	1.023	378.06	0.5827	0.7962	1.057	1.164
391.33	0.2015	0.4480	1.248	1.031	376.93	0.6268	0.8172	1.038	1.217
390.55	0.2173	0.4717	1.241	1.034	374.15	0.7404	0.8697	1.004	1.385
389.82	0.2339	0.4967	1.234	1.032	372.93	0.7996	0.8976	0.991	1.477
388.66	0.2605	0.5323	1.220	1.033	371.49	0.8623	0.9260	0.985	1.641
387.90	0.2799	0.5560	1.208	1.034	370.15	0.9309	0.9616	0.982	1.788
386.67	0.3134	0.5902	1.179	1.045	369.40	0.9675	0.9813	0.984	1.907
385.92	0.3339	0.6074	1.159	1.059	368.46	1.0000	1.0000	1.000	

tration, x_1, of the type $\rho = \sum a_i x_1^i$ derived previously, obtaining a regression coefficient, r^2, close to unity in all cases. The compositions so obtained did not differ from those calculated using the curves for excess volumes. The precision of the phase concentrations was estimated to be better than ±0.002 units of ester mole fraction.

Experimental Results

Densities and Excess Volumes. The value pairs (x_1, ρ) were determined for each of the binary systems of propyl methanoate (1) + alkan-1-ol (2) considered here, at the temperature of 298.15 K. The graphic representations of those values show the regular distribution of the excess volumes, V_m^E, for those mixtures. The values are given in Table 1; the precision of the mole fractions was $\pm 10^{-4}$, and that of the $V_m^E \pm 2 \times 10^9$ $m^3 \cdot mol^{-1}$. The V_m^E values were fitted to the ester composition using the equation

$$10^9 V_m^E/m^3 \cdot mol^{-1} = x_1 x_2 \sum_i V_i [x_1/(x_1 + k_v x_2)]^i \qquad (1)$$

The values of the coefficients V_i were obtained by the method of least squares, minimizing the standard deviations of the data, $\varsigma(V_m^E)$. The values of the parameter k_v were calculated for each mixture as the ratio between the molar volumes of the pure components (see Ortega and Alcalde, 1992). The parameter calculations are shown in Table 2. Figure 1 plots the experimental values pairs (x_1, V_m^E) and the fitting curves for the three systems considered. A search of the literature has not disclosed any V_m^E values for these mixtures, but the figure reveals a progressive increase in expansion effects in the mixtures with the number of carbon atoms in the alkan-1-ol, mainly

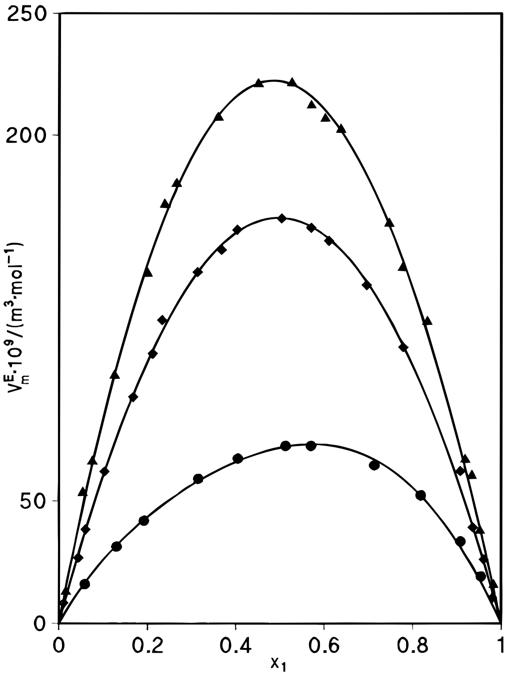

Figure 1. Experimental points and curves of V_m^E at 298.15 K for) propyl methanoate (1) + ethanol (2), (◆) propyl methanoate propan-1-ol (2), and (▲) propyl methanoate (1) + butan-1-ol

because of the steric hindrance of both components.

Vapor−Liquid Equilibria. The isobaric VLE values ${}_1-y_1$ at (160.0 ± 0.1) kPa for the mixtures considered in this study appear in Table 4, together with the values of the activity coefficients for the liquid phase, γ_i, calculated using the equation

$$\phi_i p y_i = \gamma_i p_i^o x_i \phi_i^o \exp[v_i^L(p - p_i^o)/RT] \tag{2}$$

where the fugacity coefficients, ϕ_i and ϕ_i^o, were calculated using the virial equation, truncated after the second term:

$$\phi_i = \exp[(p/RT)(2\sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij})] \tag{3}$$

The second virial coefficients for the pure components, B_{ii}, and for the mixtures, B_{ij}, were calculated using the equations proposed by Tsonopoulos (1974). Variations in the molar volumes of the liquids, v_i^L, with temperature were calculated using the version of Rackett's equation as modified by Spencer and Danner (1972). Because of the influence of the vapor pressure of the pure components, , on the thermodynamics calculations at each equilibrium state, the Antoine equation and the equation of Wagner (1973) were used to obtain the variations in p_i^o with T. The constants in the Antoine equation were the same as calculated in previous studies (Ortega et al., 1990; Galván et al., 1994). In addition, the experimental (T, p_i^o) values presented in those papers were also correlated using the equation proposed by Wagner (1973), in order to get a better representation of the vapor pressures and to observe the influence in the treatment of VLE data:

$$\ln(p_R) = (1/T_R)[a(1 - T_R) + b(1 - T_R)^{1.5} + c(1 - T_R)^3 + d(1 - T_R)^6] \tag{4}$$

where p_R was reduced pressure and T_R reduced temperature. The values of the constants a, b, c, and d obtained for the components employed are presented in Table 3. The observed differences in the vapor pressures calculated over the same temperature range using the Antoine equation and the equation of Wagner were in all cases less than 1.5%; the largest discrepancy was 6 kPa for propyl methanoate at temperatures near the boiling point of butan-1-ol at 160.0 kPa. The effect of the said correlations on the calculation of the values of γ_i yielded mean errors of less than 1% for γ_1 and less than 0.05% for γ_2 for the three

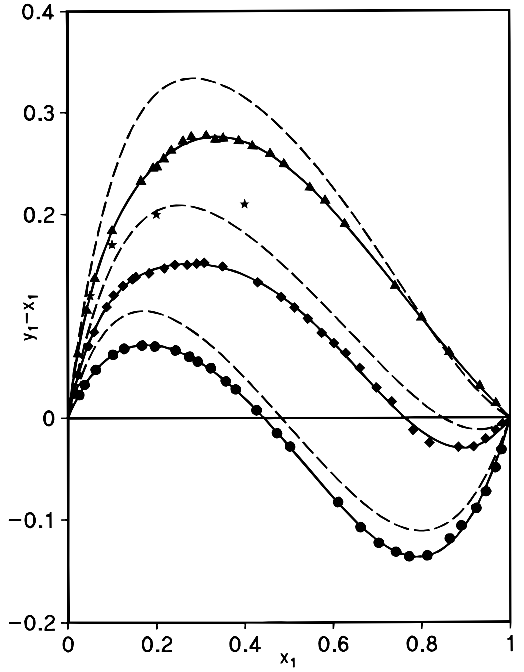

Figure 2. Experimental VLE points and curves of ($y_1 - x_1$) vs x_1 at 160.0 kPa for (●) propyl methanoate (1) + ethanol (2), (◆) propyl methanoate (1) + propan-1-ol (2), (▲) propyl methanoate (1) + butan-1-ol (2). (− − −) Corresponding curves at 101.32 kPa from Galván et al. (1994). (★) Experimental values from Mozzhukhin et al. (1967) for propyl methanoate (1) + propan-1-ol (2) at 101.32 kPa.

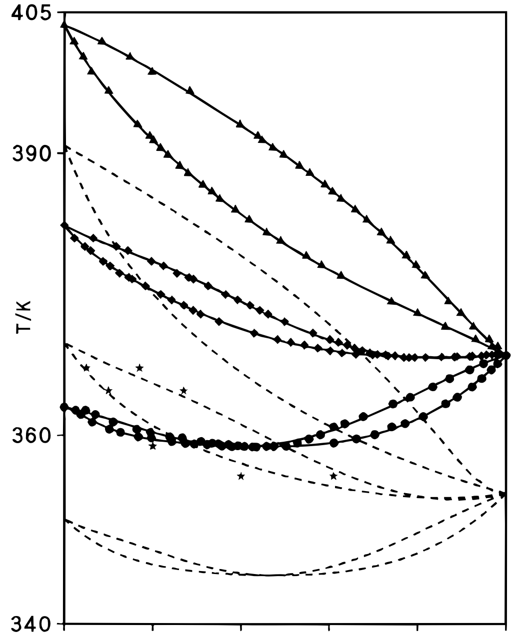

Figure 3. Experimental VLE points and curves of T vs x_1 or y_1 at 160 kPa for (●) propyl methanoate (1) + ethanol (2), (◆) propyl methanoate (1) + propan-1-ol (2), (▲) propyl methanoate (1) + butan-1-ol (2). (- - -) Corresponding curves at 101.32 kPa from Galván et al. (1994). (★) Experimental values from Mozzhukhin et al. (1967) for propyl methanoate (1) + propan-1-ol (2) at 101.32 kPa.

Table 5. Correlation Parameters for Different Equations and Standard Deviations, $\varsigma(G^E/RT)$, for Propyl Methanoate (1) + Alkan-1-ol (2) at 160.0 kPa

			$\varsigma(G^E/RT)$
Propyl Methanoate (1) + Ethanol (2)			
Margules	$A_{12} = 0.968$	$A_{21} = 0.662$	0.007
Van Laar	$A_{12} = 0.987$	$A_{21} = 0.687$	0.007
Wilson	$\Delta\lambda_{12} = 1161.4$ J·mol^{-1}	$\Delta\lambda_{21} = 1856.1$ J·mol^{-1}	0.007
NRTL ($\alpha = 0.83^a$)	$\Delta g_{12} = 1619.8$ J·mol^{-1}	$\Delta g_{21} = 416.9$ J·mol^{-1}	0.007
UNIQUAC ($z = 10$)	$\Delta u_{12} = -73.1$ J·mol^{-1}	$\Delta u_{21} = 985.1$ J·mol^{-1}	0.007
Redlich−Kister	$A_0 = 0.815$	$A_1 = -0.153$	0.007
eq 5 ($k = 13.08$)	$A_0 = 0.893$	$A_1 = -0.775$	0.005
Propyl Methanoate (1) + Propan-1-ol (2)			
Margules	$A_{12} = 0.697$	$A_{21} = 0.637$	0.006
Van Laar	$A_{12} = 0.696$	$A_{21} = 0.640$	0.006
Wilson	$\Delta\lambda_{12} = 571.3$ J·mol^{-1}	$\Delta\lambda_{21} = 1715.2$ J·mol^{-1}	0.006
NRTL ($\alpha = 1.44^a$)	$\Delta g_{12} = 955.9$ J·mol^{-1}	$\Delta g_{21} = 747.3$ J·mol^{-1}	0.006
UNIQUAC ($z = 10$)	$\Delta u_{12} = -51.8$ J·mol^{-1}	$\Delta u_{21} = 709.8$ J·mol^{-1}	0.006
Redlich−Kister	$A_0 = 0.667$	$A_1 = -0.030$	0.006
eq 5 ($k = 8.60$)	$A_0 = 0.700$	$A_1 = -0.253$	0.005
Propyl Methanoate (1) + Butan-1-ol (2)			
Margules	$A_{12} = 0.383$	$A_{21} = 0.421$	0.004
Van Laar	$A_{12} = 0.382$	$A_{21} = 0.424$	0.004
Wilson	$\Delta\lambda_{12} = 371.0$ J·mol^{-1}	$\Delta\lambda_{21} = 974.1$ J·mol^{-1}	0.004
NRTL ($\alpha = 6.02^a$)	$\Delta g_{12} = 442.7$ J·mol^{-1}	$\Delta g_{21} = 446.7$ J·mol^{-1}	0.004
UNIQUAC ($z = 10$)	$\Delta u_{12} = -234.2$ J·mol^{-1}	$\Delta u_{21} = 635.7$ J·mol^{-1}	0.004
Redlich−Kister	$A_0 = 0.402$	$A_1 = 0.019$	0.004
eq 5 ($k = 4.09$)	$A_0 = 0.387$	$A_1 = 0.070$	0.004

By fit.

Table 6. Coefficients a_i, b_i, and k_g in Eqs 6 and 9 and Standard Deviations, $\varsigma(\gamma_i)$

mixture	k_g	a_0	a_1	b_0	$\varsigma(\gamma_i)$
propyl methanote (1) + ethanol (2)	0.18	0.861		−0.115	0.017
propyl methanoate (1) + propan-1-ol (2)	1.31	0.686	0.209	−0.599	0.033
propyl methanoate (1) + butan-1-ol (2)	3.21	0.509	0.226	−0.477	0.019

Table 7. Parameters Obtained for Eq 5 and Standard Deviations, $\varsigma(Q_k)$, of the Different Correlations

correlation	k	A_0	A_1	A_2	A_3	$\varsigma(Q_k)$
Propyl Methanoate (1) + Ethanol (2)						
vs x_1	0.64	1.039	−2.888	3.680	−3.332	0.002
vs x_1	0.27	−21.46	−79.28	204.95	−145.20	0.09
vs y_1	0.85	−14.55	−53.04	59.04		0.16
Propyl Methanoate (1) + Propan-1-ol (2)						
vs x_1	0.54	2.070	−5.967	9.163	−5.867	0.002
vs x_1	0.37	−46.75	91.23	−127.58	67.61	0.08
vs y_1	0.72	−13.44	63.18	−171.60	106.17	0.11
Propyl Methanoate (1) + Butan-1-ol (2)						
vs x_1	0.28	3.335	−6.400	7.395	−3.928	0.002
Q_3 vs x_1	0.52	−55.01	101.20	−122.18	65.00	0.09
Q_4 vs y_1	1.45	16.51	−32.73	106.32	−89.88	0.11

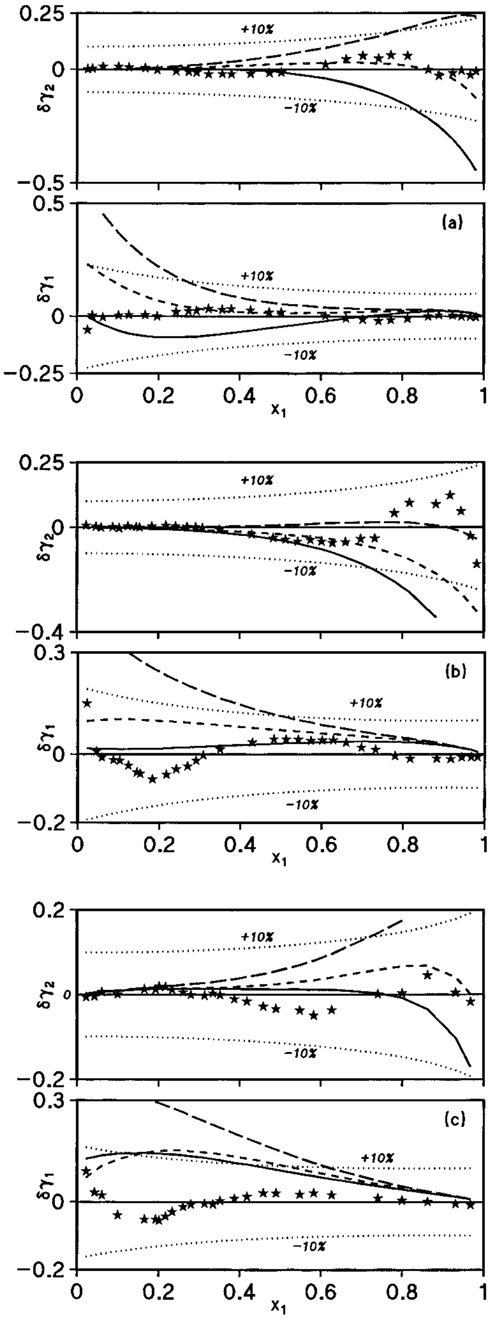

Figure 4. (a−c) Deviations, $\delta\gamma_i(\gamma_i^{est} - \gamma_i^{eq5})$, between the estimated theoretical values and those obtained by eq 5: (—) ASOG from Tochigi et al. (1990); (− − −) UNIFAC from Hansen et al. (1991); (- - -) UNIFAC from Gmehling et al. (1993). The symbols (★) represent the difference between experimental values and those obtained by eq 5.

mixtures considered, thereby validating the use of both these equations in the calculations. At high concentrations the mixtures present a slight negative deviation from ideality and negative values for G^E/RT because of experimental error to get mixtures richer in ester in the vapor phase. The values in Table 4 were shown to be consistent by using the version of the point-to-point test proposed by Fredenslund et al. (1977) in which the subroutines for calculating the virial coefficients and the molar volumes of the pure liquids and the mixtures were modified as already described above.

The literature only disclosed isobaric VLE values for these three mixtures at 101.32 kPa, recently published by our laboratory (Galván et al., 1994) and those published by Mozzhukhin et al. (1967) for the system propyl methanoate + propan-1-ol. Figures 2 and 3 contain a qualitative comparison of the values at 160.0 kPa presented herein and the literature values at $p = 101.32$ kPa.

Correlation of the VLE Values. The adimensional function for the Gibbs energy, G^E/RT, obtained from the γ_i values set out in Table 4 was correlated for each mixture using the classic models of van Laar, Margules, Wilson, and Redlich−Kister, the NRTL and UNIQUAC models, and a polynomial equation similar to eq 1 above. This last-mentioned equation had already yielded good results in the correlation of the excess magnitudes in the earlier work on VLE values carried out by our laboratory. The equation takes the form

Table 8. Average Percent Errors $e(\gamma)$, Mean Deviations $\delta(y_1)$ and Azeotropic Data Obtained in the Prediction of VLE for the Mixtures Propyl Methanoate (1) + Alkan-1-ol (2) Using Different Group-Contribution Models

	ASOG	UNIFAC			mod-UNIFAC
	OH/COO[a]	OH/HCOO[b]	COH/COO[c]	OH/COO[d]	OH/HCOO[e]
		Propyl Methanoate (1) + Ethanol (2)			
$e(\gamma)$	4.7	6.6	2.1	5.1	2.5
$\delta(y_1)$	0.017	0.010	0.007	0.017	0.007
$\delta(T)$	0.5	1.2	0.2	0.6	0.4
azeotrope(x_1, T/K)	(0.390, 359.4)	(0.437, 357.4)	(0.424, 358.6)	(0.407, 359.7)	(0.424, 358.3)
		Propyl Methanoate (1) + Propan-1-ol (2)			
$e(\gamma)$	4.1	6.7	5.1	5.4	4.3
$\delta(y_1)$	0.011	0.021	0.017	0.012	0.014
$\delta(T)$	0.2	1.5	0.9	0.5	0.7
Azeotrope(x_1, T/K)	(0.910, 368.1)	(0.793, 366.9)	(0.825, 367.4)	(0.943, 368.2)	(0.841, 367.6)
		Propyl Methanoate (1) + Butan-1-ol (2)			
$e(\gamma)$	5.3	10.5	9.8	3.6	5.7
$\delta(y_1)$	0.019	0.033	0.031	0.011	0.020
$\delta(T)$	1.7	3.1	2.9	0.7	2.0

$$e(\gamma) = (1/2)\sum_{i=1}^{2}\sum_{j=1}^{N}|(\gamma_{i,j}^{\rm exp} - \gamma_{i,j}^{\rm cal})/\gamma_{i,j}^{\rm exp}|100/N;\ \delta(y_1) = \sum_{j=1}^{N}|y_{1,j}^{\rm exp} - y_{1,j}^{\rm cal}|/N;\ \delta(T) = \sum_{j=1}^{N}|T_j^{\rm exp} - T_j^{\rm cal}|/N$$

$$Q_k = x_1x_2\sum_i A_i[x_1/(x_1 + kx_2)]^i \qquad (5)$$

where Q_k was the function to be fitted. The values of the coefficients A_i were calculated by means of a least-squares procedure based on minimization of the standard deviation,), for each value of k. Table 5 gives the values of the coefficients and the standard deviations for the correlation of the values for $Q_1 = G^E/RT$ on x_1 using the above-mentioned models. According to the results, all the equations used would appear to be equally suitable.

An equation similar to eq 5 was used to simultaneously fit the values of Q_1 and the activity coefficients, which are related using

$$_1 = Q_1 + x_2 \ln(\gamma_1/\gamma_2) \quad \text{and} \quad \ln \gamma_2 = Q_1 - x_1 \ln(\gamma_1/\gamma_2) \qquad (6)$$

Equation 5 yields a good approximation of the function Q_1, while the term $\ln(\gamma_1/\gamma_2)$ under isobaric conditions, which can be expressed as

$$\ln(\gamma_1/\gamma_2)_{\rm p} = (\partial Q_1/\partial x_1)_{\rm p} + (h^{\rm E}/RT)(\partial T/\partial x_1)_{\rm p} \qquad (7)$$

was replaced by a simplified form of eq 5. Chao (1959) made a similar modification in the Redlich–Kister equation. This yielded the following generic expression of eq

$$\frac{1}{2} = (1 - 2x_1)(\sum_i a_iz^i) + x_1x_2k_{\rm g}(z/x_1)^2(\sum_i(i + 1)z^ia_{i+1}) + x_1x_2(\sum_i b_ix_1^i) \qquad (8)$$

where, the subscript "g" indicates the correlation of the free energy function and $z = x_1/(x_1 + k_{\rm g}x_2)$. This equation is simpler when only a limited number of coefficients is considered. Thus, for the first two coefficients a_i and a single coefficient b_i

$$\ln\frac{\gamma_1}{\gamma_2} = (1 - 2x_1)(a_0 + a_1z) + x_1x_2(a_1k_{\rm g}(z/x_1)^2 + b_0) \qquad (9)$$

As in the case of the equation proposed by Chao (1959), because of the influence of the new constants employed, the coefficients a_i and $k_{\rm g}$ are no longer the equivalents of the coefficients A_i and k in eq 5 obtained above for the adimensional function for the Gibbs free energy (see Table 5). In this case, to obtain the coefficients in eq 9, the following objective function was optimized:

$$\mathrm{OF} = \sum_i(\gamma_{1,i}^{\rm exp} - \gamma_{1,i}^{\rm cal})^2 + \sum_i(\gamma_{2,i}^{\rm exp} - \gamma_{2,i}^{\rm cal})^2 \qquad (10)$$

The parameters in eq 8 or eq 9 so obtained have been set out in Table 6 together with the mean standard deviation for the values of γ_1 and γ_2, defined as $\varsigma(\gamma_i) = 0.5[\varsigma(\gamma_1)^2 + \varsigma(\gamma_1)^2]^{1/2}$. The standard deviations for the adimensional magnitude G^E/RT were the same as for the direct correlations shown in Table 5; hence eq 9 would appear to be more suitable for use in simultaneous correlations of the free energy and the activity coefficients. In Figure 4a–c each curve was transformed into the abscissa axis, and the differences between the experimental values of γ_i and the values calculated using the above-mentioned correlations were plotted for each of the mixtures considered.

The equilibrium values for composition and temperature were also correlated using eq 5 for the functions $Q_2 = y_1 - x_1$, $Q_3 = T - \sum x_iT_{{\rm b},i}$, and $Q_4 = T - \sum y_iT_{{\rm b},i}$. Table 7 presents the values of the coefficients obtained for each of the said functions and the respective standard deviations, $\varsigma(Q_k)$. Figures 2 and 3 graphically represent the fitting curves obtained using the above functions Q_2, Q_3, and Q_4.

Azeotropes. Two of the mixtures considered presented singular points at a minimum boiling temperature. Propyl methanoate (1) + ethanol (2) presented an azeotrope at $T = 358.7$ K, $x_1 = y_1 = 0.443$ and propyl methanoate (1) + propan-1-ol (2) at $T = 368.2$ K, $x_1 = y_1 = 0.762$. Comparing the coordinates for the azeotropes with the values published in the literature for the same mixtures at $p = 101.32$ kPa (Galván et al., 1994), one can observe that the decrease of the working pressure employed shifts the azeotropes to higher ester concentrations and lower temperature values.

Prediction of VLE Using Different Group-Contribution Models. The activity coefficients, γ_i, and the compositions of the vapor phase, y_1, from Table 4 were compared to the predictions obtained using group-contribution methods, namely, the ASOG model (Tochigi et al., 1990), the UNIFAC model (Fredenslund et al., 1975), and a modified version of the UNIFAC model (Gmehling et al., 1993). The modified-UNIFAC model proposed by Larsen et al. (1987) does not contain specific parameter values for the interaction pair HCOO/G, where G is a generic functional group. Table 8 contains a quantitative comparison of the theoretical estimates, showing the mean overall errors for the γ_i values and the mean differences for the y_1 values for the entire range of experimental data points together with the maximum differences obtained for y_1.

On the whole, the modified version of the UNIFAC model (Gmehling et al., 1993) yielded the best prediction of the γ_i values, with a mean error of 4% for the three systems considered taken together. The ASOG model also yielded excellent predictions, with a mean error of less than 5% for the γ_i values. The mean error in the values of the γ_i obtained using the version of the UNIFAC model of Fredenslund et al. (1975) depended upon the interaction pair considered and ranged from 8% for the OH/HCOO interaction to 5% for the OH/COO interaction parameters published by Macedo et al. (1983), although recommended for non-alkyl esters. Parts a−c of Figure 4 graphically represent the differences between the experimental curves for the activity coefficients from Table 6 and the theoretical values predicted by the ASOG model and the two versions of the UNIFAC model for all three mixtures considered. For all three models and systems, a common characteristic appears: the discrepancies in the γ_i values decrease in the respective regions with rich concentrations of component

All the theoretical models employed in this study confirmed the presence of an azeotrope in the binary mixtures formed by propyl methanoate + ethanol and propyl methanoate + propan-1-ol at 160.0 kPa. Quantitatively, the version of the UNIFAC model by Gmehling et al. (1993) yielded the best estimate of the singular point for the mixture propyl methanoate (1) + ethanol (2), at $x_1 = y_1 = 0.424$, $T = 358.3$ K, though those values were quite similar to the values obtained using the original UNIFAC model employing the interaction pair COH/COO. However, the azeotrope for propyl methanoate (1) + propan-1-ol (2) was not predicted well with the models used herein.

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