Experimental Determination of Densities and Isobaric Vapor−Liquid Equilibria of Binary Mixtures Formed by a Propyl Alkanoate (Methanoate to Butanoate) + An Alkan-2-ol (C_3, C_4)

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Vapor−liquid equilibria at 101.32 kPa of binary systems composed of the first four propyl esters, from methanoate to butanoate, and propan-2-ol or butan-2-ol and the vapor pressures of the pure components were measured in the same equilibrium still. The densities and excess volumes for the same mixtures were also determined at 298.15 K. The binary systems studied presented a positive deviation from ideality, and four of the mixtures had azeotropes at the working pressure, namely, propyl methanoate (1) + propan-2-ol (2) at $x_1 = 0.570$ and $T = 349.4$ K, propyl methanoate (1) + butan-2-ol (2) at $x_1 = 0.933$ and $T = 353.6$ K, propyl ethanoate (1) + propan-2-ol (2) a $x_1 = 0.037$ and $T = 355.2$ K, and propyl ethanoate (1) + butan-2-ol (2) at $x_1 = 0.423$ and $T = 370.8$ K. The isobaric VLE quantities were correlated together with the mixing enthalpies obtained for the corresponding mixtures using a suitable equation containing temperature-dependent parameters. The ASOG and UNIFAC group-contribution models were used to predict the VLE values.

Introduction

Earlier papers (Galván et al., 1994; Ortega and Galván, 1994, 1995; Falcón et al., 1996) have reported isobaric vapor equilibrium (VLE) values for binary mixtures composed of the first four propyl esters (methanoate to butanoate) and normal alkanols (ethanol to butan-1-ol). To complete the experimental database in preparation at our laboratory, isobaric VLE values have been measured for mixtures of those same propyl esters with propan-2-ol and butan-2-ol at a pressure of 101.32 kPa. In the literature consulted, Gmehling et al. (1977, Vol. I, part 2f, p 225) compiled isothermal VLE values for the mixture consisting of propyl ethanoate + butan-2-ol at $T = 313$ K. In addition, the azeotropic database released by Gmehling et al. (1994) contains the azeotropic coordinates (x_{az}, T_{az}) for the singular points of the mixtures consisting of propyl methanoate + propan-2-ol (0.548, 349.1) and propyl ethanoate + butan-2-ol (0.392, 370.5) at atmospheric pressure. For this same mixture, the above-mentioned isothermal study yielded an azeotropic point at an ester concentration of 0.796 and a pressure of 10.4 kPa.

This paper also presents values for other excess thermodynamic quantities, V_m^E and H_m^E, for the mixtures considered with a view to contributing to our understanding of their behavior. The values for those quantities and the VLE values were correlated using a suitable equation already employed in previous work by Soto et al. (1998).

Predictions of the values published here were also calculated using the original UNIFAC model with the parameters by Hansen et al. (1991), a modified version of the UNIFAC model with the interaction values provided by Gmehling et al. (1993), and the ASOG model with the parameters published by Tochigi et al. (1990).

Experimental Section

Chemicals. Esters and alkanols were supplied by Fluka and Aldrich and were the highest purity commercial grade. Before use all components were degassed by ultrasound and then dried in darkness over molecular sieves (Fluka, 0.3 nm). The manufacturer's purity specification was verified using an HP-6890 GC equipped with an HP-Wax capillary column and an FID, and no significant impurities were found. Table 1 summarizes the manufacturer's specifications and certain properties for the chemicals used in this study, namely, the normal boiling point $T_{b,i}^{\circ}$, as well as the density ρ and the refractive index n(D) at 298.15 K.

Equipment and Procedure. The equilibrium experimentation was performed using a small-capacity equilibrium still described previously (Ortega and Susial, 1991). Temperature measurements were taken using a Comark Electronics Ltd. model 6800 digital thermometer with platinum sensors periodically calibrated with respect to the ITS-90 using a standard ASL-F25 thermometer. The estimated uncertainty of the reading was 0.02%. The working pressure was regulated using a Desgranges et Huot (France), model PPC2, controller/calibration unit, with a maximum error in the reading of ±0.02 kPa.

The composition of each of the phases at vapor−liquid equilibrium was determined using the density−ester mole fraction correlations x, $\rho = \sum a_i x^i$ obtained for each of the mixtures previously. The densimetric measurements of mixtures, specially prepared for the purpose of calibration, and those corresponding to the liquid and vapor phases were carried out using an Anton-Paar model DMA-55 densimeter with a precision of ± 0.02 kg·m^{-3}. The sample temperature was regulated to 298.15 K with a variation of less than ±0.02 K. Simple polynomial expressions were used to calculate the ester concentration for each of the phases. The accuracy of the calculations were estimated to be better than ±0.002 mole fraction units.

Results and Discussion

Densities and Excess Volumes. The densities for the binary mixtures considered in this study were measured

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Table 1. Physical Properties of Pure Compounds Measured at Atmospheric Pressure

	n(D, 298.15 K)		ρ(298.15)/kg·m^{-3}		$T^{\circ}_{b,i}$		ω	
compound	this work	lit.	this work	lit.	this work	lit.	this work	lit.
propan-2-ol	1.3752	1.3752[a] 1.37527[b]	781.33	781.26[a] 780.82[b]	355.30	355.41[a] 355.48[b]	0.664	0.669[c]
butan-2-ol	1.3949	1.3950[a] 1.3949[b]	802.58	802.60[a] 802.30[b]	372.27	372.65[b]	0.568	0.571[c]
propyl methanoate	1.3744	1.3750[a,b]	899.29	899.60[a,b] 898.86[c]	353.75	353.97[a–c]	0.309	0.318[c]
propyl ethanoate	1.3816	1.3828[a–c] 1.3817[d]	882.67	883.03[a] 882.60[b,c]	374.31	374.69[a] 374.65[b,c]	0.391	0.394[c]
propyl propanoate	1.3906	1.3920[b,c]	875.61	876.70[b] 876.82[c]	395.56	395.65[b,c] 395.30[e]	0.376	0.376[c]
propyl butanaote	1.3975	1.3976[b,c]	868.01	868.20[b] 868.04[c]	416.57	416.45[b,c] 416.74[e]	0.449	0.448[c]

[a] Riddick et al. (1986). [b] TRC (1993). [c] Daubert and Danner (1984). [d] Timmermans (1965). [e] Fárková and Wichterle (1993).

Table 2. Experimental Densities ρ and Excess Volumes V_m^E at T = 298.15 K for Binary Mixtures of Propyl Esters (1) + Alkan-2-ol (2)

x_1	ρ/kg·m^{-3}	$10^9 V_m^E$/m^3·mol^{-1}	x_1	ρ/kg·m^{-3}	$10^9 V_m^E$/m^3·mol^{-1}	x_1	ρ/kg·m^{-3}	$10^9 V_m^E$/m^3·mol^{-1}
			Propyl Methanoate (1) + Propan-2-ol (2)					
0.000	781.33	0	0.286	818.51	301	0.612	857.02	345
0.108	796.04	141	0.345	825.73	331	0.706	867.41	310
0.110	796.42	143	0.349	826.29	326	0.769	874.37	273
0.163	803.26	197	0.408	833.24	355	0.832	881.31	212
0.224	810.76	261	0.475	841.21	363	0.915	890.19	121
0.225	810.99	257	0.540	848.78	357	1.000	899.29	0
			Propyl Ethanoate (1) + Propan-2-ol (2)					
0.000	781.33	0	0.373	825.82	378	0.644	852.22	388
0.095	793.86	141	0.434	832.05	409	0.736	860.47	334
0.148	800.42	210	0.495	838.10	418	0.811	866.98	267
0.195	805.93	265	0.506	839.19	422	0.888	873.56	168
0.248	812.13	304	0.573	845.61	414	1.000	882.67	0
0.308	818.85	344	0.580	846.25	412			
			Propyl Propanoate (1) + Propan-2-ol (2)					
0.000	781.33	0	0.285	817.22	278	0.702	854.46	321
0.028	785.38	29	0.338	822.80	304	0.783	860.54	275
0.042	787.45	47	0.394	828.36	331	0.872	866.94	183
0.083	793.07	95	0.469	835.32	349	0.880	867.34	177
0.087	793.31	98	0.535	841.21	354	0.928	870.70	119
0.112	796.83	137	0.543	841.67	354	0.940	871.46	99
0.177	804.93	203	0.621	848.29	349	1.000	875.61	0
0.233	811.50	246	0.702	854.55	322			
			Propyl Butanoate (1) + Propan-2-ol (2)					
0.000	781.33	0	0.261	814.62	258	0.691	849.87	318
0.036	786.83	39	0.310	819.47	291	0.766	854.63	282
0.076	792.56	81	0.368	825.00	319	0.863	860.47	194
0.120	798.40	132	0.437	831.07	341	0.945	865.15	92
0.161	803.38	176	0.493	835.63	352	1.000	868.01	0
0.207	808.68	216	0.584	842.49	353			
			Propyl Methanoate (1) + Butan-2-ol (2)					
0.000	802.58	0	0.321	830.56	485	0.720	869.44	424
0.032	805.27	61	0.388	836.87	515	0.786	876.15	366
0.065	807.91	138	0.448	842.52	536	0.864	884.37	259
0.127	813.12	268	0.520	849.48	536	0.925	890.91	157
0.193	818.94	353	0.589	856.20	520	0.951	893.82	107
0.263	825.18	439	0.653	862.57	485	1.000	899.29	0
			Propyl Ethanoate (1) + Butan-2-ol (2)					
0.000	802.58	0	0.321	828.01	517	0.710	859.07	473
0.063	807.38	170	0.392	833.72	552	0.791	865.43	388
0.101	810.34	244	0.447	838.14	564	0.813	867.20	357
0.147	814.09	322	0.524	844.28	564	0.854	870.52	297
0.212	819.27	412	0.577	848.50	554	0.906	874.64	212
0.229	820.66	431	0.646	854.02	517	1.000	882.67	0
0.282	824.92	480	0.674	856.21	500			
			Propyl Propanoate (1) + Butan-2-ol (2)					
0.000	802.58	0	0.219	820.62	361	0.572	847.00	494
0.060	807.65	132	0.267	824.42	407	0.608	849.45	487
0.061	807.74	134	0.306	827.43	440	0.715	856.77	426
0.073	808.78	154	0.383	833.28	481	0.859	866.28	272
0.130	813.47	246	0.417	835.84	495	0.935	871.33	139
0.160	815.91	291	0.449	838.21	499	1.000	875.61	0
0.171	816.81	309	0.515	842.96	505			
			Propyl Butanoate (1) + Butan-2-ol (2)					
0.000	802.58	0	0.363	830.58	465	0.714	852.26	419
0.080	809.33	158	0.385	832.06	473	0.784	856.11	359
0.110	811.86	204	0.516	840.53	498	0.836	859.00	292
0.162	816.04	273	0.574	844.13	485	0.881	861.42	232
0.206	819.30	336	0.542	842.18	492	0.968	866.08	75
0.257	823.11	381	0.681	850.37	445	1.000	868.01	0

Table 3. Molar Volumes V_i° for Pure Compounds at 298.15 K, Coefficients b_i, and $k_v = V_2^\circ/V_1^\circ$, and Standard Deviations, $s(V_m^E)$ Obtained Using Eq 1 To Correlate Excess Volumes of Binary Mixtures of Propyl Esters (1) + Alkan-2-ol (2)

mixture	$10^6V_i^\circ$/m³·mol⁻¹	k_v	b_0	b_1	b_2	$10^9s(V_m^E)$/m³·mol⁻¹
propan-2-ol (2) +	76.97[a]					
propyl methanoate (1)	97.97[a]	0.786	1535	−371	413	4
propyl ethanoate (1)	115.71[a]	0.665	1588	146		5
propyl propanoate (1)	132.66[a]	0.580	1388	−413	748	6
propyl butanoate (1)	149.99[a]	0.513	1264	−48	442	5
butan-2-ol (2) +	92.38[a]					
propyl methanoate (1)	97.97[a]	0.943	2484	−988	773	6
propyl ethanoate (1)	115.71[a]	0.798	2909	−2148	1772	3
propyl propanoate (1)	132.66[a]	0.696	2443	−1553	1425	3
propyl butanoate (1)	149.99[a]	0.616	2265	−1109	1074	5

[a] Calculated using the densities from Table 1.

at the temperature (298.15 ± 0.01) K for a set of mixtures prepared with different propyl ester concentrations. The results (x, ρ) for each ester mole fraction were estimated to a precision of ±0.0001 units in the concentration and are presented in Table 2 together with the values obtained for densities and for excess volumes, V_m^E. The imprecision in the calculations for that excess quantity was better than $\pm 2 \times 10^{-9}$ m³·mol⁻¹. Experimental values for the mixtures of a propyl alkanoate (1) + an alkan-2-ol (2) were correlated using the polynomial equation

$$10^9\ V_m^E/(\text{m}^3\cdot\text{mol}^{-1}) = x_1x_2\sum b_iz^i \qquad (1)$$

where $z = x_1/(x_1 + k_vx_2)$, in which the coefficients b_i were calculated by a least squares procedure minimizing the standard deviation of the data, $s(V_m^E)$. The values of the parameter k_v were held constant for each mixture as proposed by Ortega and Alcalde (1992). The values of k_v were obtained by dividing the molar volumes of the pure components of the binary mixtures, V_1°/V_2° at the same working temperature calculated using the density values presented in Table 1. Table 3 contains the values for the coefficients b_i obtained for each binary mixture in eq 1. Those values were used to plot the curves for that magnitude in Figure 1. The plots show the expansion effects in the mixtures considered but do not exhibit uniform variation in the V_m^E values with propyl ester chain length or molecular weight for a given alkan-2-ol. However, the boxes inset in Figure 1, which display curves constructed using the values for the equimolar mixtures, $V_m^E(x_1 = 0.5)$, for the propyl ester used in this study situated between curves for mixtures containing ethyl and butyl esters used in previous studies (Hernandez and Ortega, 1997; Gonzalez and Ortega, 1996a, 1996b), did more clearly reflect the variation which represents the behavior of the mixture. The most interesting finding which can be discerned from the figures was the lower than expected values for the mixtures containing alkyl methanoates, indicative of significant specific coupling, probably caused by the formation of methanoate−alkanol complexes. This contributes negatively to the V_m^E values and exerts a certain exothermic effect on the mixing process, resulting in a decrease in the net values of the excess quantities. Nevertheless, the net effects for both V_m^E and H_m^E values were positive because the effects of bond rupture and weakening of polar forces (resulting in considerable steric hindrance) predominated over the negative effects just described.

Pure Component Vapor Pressures. The vapor pressure determinations were carried out using the same equilibrium still and auxiliary equipment already referred to above. The data pairs collected (T, p_i°) for the six propyl esters and alkan-2-ols employed in this study are given in Table 4. In previous papers, Ortega and Galván (1994, 1995) presented the vapor pressures for propyl propanoate and propyl butanoate, but since the values published

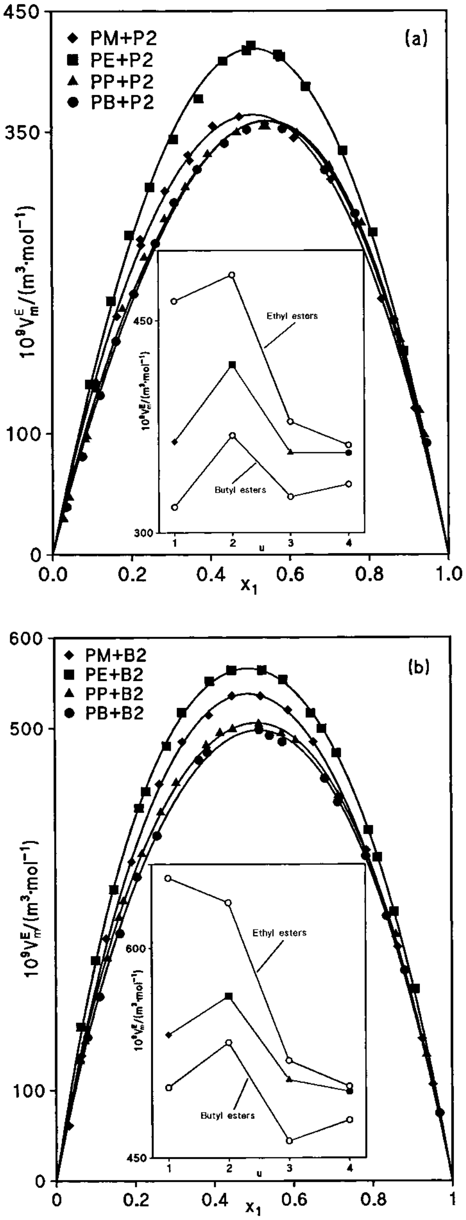

Figure 1. Experimental points and curves obtained at 298.15 K for V_m^E of binary mixtures formed by propyl esters (1), $C_{u-1}H_{2u+1}CO_2C_3H_7$, with alkan-2-ols (2): (a) propan-2-ol (P2); (b) butan-2-ol (B2). Inset figures correspond to comparison of $V_m^E(x_1 = 0.5)$ values found in this work for propyl esters (1) + alkan-2-ol (2) and those published for the mixtures containing ethyl esters from Hernandez and Ortega (1997) and butyl esters from Gonzalez and Ortega (1996a,b).

Table 4. Experimental Vapor Pressures for Pure Propyl Esters and Alkan-2-ols

T/K	p_i^o/kPa	T/K	p_i^o/kPa	T/K	p_i^o/kPa	T/K	p_i^o/kPa	T/K	p_i^o/kPa	T/K	p_i^o/kPa
Propan-2-ol											
339.01	50.62	347.89	74.66	352.23	89.41	355.98	104.00	359.93	121.32	363.41	138.62
340.42	53.92	348.31	75.97	352.58	90.66	356.30	105.32	360.22	122.66	363.94	141.40
341.80	57.37	348.73	77.36	352.94	92.06	356.62	106.66	360.50	124.00	364.42	144.01
343.32	61.31	349.13	78.66	353.31	93.42	357.55	110.65	360.75	125.22	364.89	146.53
344.29	63.97	349.54	79.99	353.67	94.73	357.86	111.99	361.04	126.62	365.38	149.25
345.23	66.62	349.92	81.30	354.03	96.06	358.19	113.29	361.29	127.85	365.89	152.12
345.69	67.97	350.32	82.62	354.36	97.34	358.49	114.66	361.58	129.27	366.34	154.65
346.16	69.32	350.74	84.08	354.70	98.69	358.78	115.99	361.88	130.78	366.80	157.32
346.60	70.64	351.13	85.43	355.02	99.98	359.07	117.32	362.10	131.88	367.18	159.53
347.04	71.99	351.49	86.74	355.30	101.32	359.37	118.65	362.37	133.26	367.52	161.54
347.47	73.33	351.86	88.05	355.66	102.66	359.65	119.99	362.91	136.00		
Butan-2-ol											
353.35	47.60	367.34	83.97	371.56	98.66	374.33	109.33	376.55	118.70	380.43	136.24
354.96	51.00	367.74	85.31	371.92	99.95	374.63	110.55	376.87	120.02	380.92	138.55
357.17	56.02	368.14	86.66	372.27	101.32	374.98	112.09	377.14	121.29	381.48	141.28
359.59	61.86	368.55	88.00	372.65	102.92	374.99	111.99	377.48	122.68	382.01	143.92
361.59	67.04	368.95	89.38	372.94	104.05	375.28	113.42	378.10	125.48	382.59	146.79
362.17	68.69	369.27	90.49	372.99	104.00	375.29	113.20	378.37	126.63	383.10	149.33
364.13	74.01	369.72	92.05	373.32	105.28	375.61	114.70	378.66	128.01	383.60	151.95
365.11	77.07	370.08	93.33	373.61	106.64	375.62	114.61	378.96	129.33	384.10	154.71
366.11	80.07	370.45	94.64	373.67	106.65	375.91	115.96	379.25	130.77	384.60	157.31
366.53	81.40	370.83	96.00	373.99	107.94	375.94	115.91	379.52	131.88	384.86	158.75
366.94	82.68	371.19	97.32	374.32	109.43	376.21	117.28	379.81	133.33	385.35	161.48
Propyl Methanoate											
327.99	40.48	337.86	58.65	345.73	77.32	351.80	94.66	358.31	116.49	363.95	138.52
328.87	41.86	338.47	59.99	346.23	78.65	352.25	95.97	358.64	117.70	364.60	141.29
329.69	43.20	339.09	61.33	346.72	79.99	352.67	97.31	359.04	119.17	365.24	143.99
330.53	44.64	339.68	62.65	347.17	81.20	353.09	98.63	359.44	120.64	365.86	146.62
331.27	45.92	340.28	63.99	347.65	82.52	353.75	101.32	359.96	122.58	366.45	149.30
332.08	47.33	340.92	65.44	348.13	83.86	354.49	103.21	360.31	123.98	367.05	151.95
332.87	48.78	341.44	66.66	348.65	85.32	354.94	104.68	360.66	125.31	367.64	154.62
333.82	50.51	341.99	67.99	349.12	86.65	355.39	106.18	360.99	126.64	368.21	157.20
334.52	51.83	342.55	69.32	349.51	87.81	355.81	107.63	361.33	127.96	368.80	159.91
335.11	53.03	343.10	70.65	350.04	89.30	356.29	109.35	361.67	129.31	369.35	162.55
335.97	54.79	343.64	71.99	350.48	90.66	356.70	110.73	362.01	130.64	369.90	165.15
336.58	55.99	344.16	73.32	350.92	91.96	357.25	112.63	362.35	131.96	370.61	168.53
337.23	57.32	344.70	74.65	351.38	93.32	357.64	114.02	362.65	133.24		
Propyl Ethanoate											
354.86	53.33	367.51	81.34	373.29	97.42	376.22	106.73	380.52	121.33	385.13	138.78
356.27	55.98	368.02	82.67	373.68	98.60	376.61	107.99	380.87	122.57	385.77	141.32
357.63	58.68	369.03	85.36	374.22	100.28	377.02	109.36	381.28	124.09	386.44	144.05
358.94	61.36	369.52	86.69	374.31	101.32	377.45	110.75	381.64	125.38	387.08	146.71
360.19	64.01	370.02	88.04	374.57	101.41	377.85	112.09	381.98	126.67	387.84	149.92
361.37	66.59	370.49	89.36	374.60	101.44	378.25	113.41	382.35	128.09	388.65	153.48
362.59	69.35	370.98	90.69	374.61	101.64	378.59	114.61	382.67	129.28	389.41	156.88
363.72	71.97	371.46	92.07	374.96	102.68	379.03	116.10	383.07	130.79	390.13	160.13
364.85	74.66	371.90	93.36	375.39	103.96	379.44	117.52	383.41	132.14	391.06	164.38
365.93	77.33	372.38	94.72	375.39	104.06	379.75	118.61	383.75	133.30		
367.00	80.02	372.88	96.16	375.78	105.33	380.15	120.00	384.40	135.86		
Propyl Propanoate											
366.55	39.98	381.23	65.35	389.80	85.35	397.35	106.60	403.07	125.43	408.48	145.43
368.24	42.42	381.85	66.66	390.32	86.67	397.78	107.90	403.46	126.75	408.80	146.75
369.34	43.99	382.50	68.03	390.81	88.00	398.21	109.23	403.83	128.08	409.06	147.70
370.45	45.73	383.10	69.35	391.32	89.31	398.67	110.65	404.23	129.42	409.48	149.41
371.78	47.85	383.72	70.75	391.82	90.68	399.04	111.89	404.58	130.77	409.83	150.76
372.99	49.85	384.32	72.02	392.31	92.00	399.10	112.11	404.95	132.08	410.14	152.04
374.96	53.27	384.87	73.31	392.79	93.33	399.49	113.39	405.31	133.41	410.48	153.43
375.91	54.87	385.45	74.66	393.75	96.01	399.95	114.76	405.68	134.76	410.76	154.67
376.57	56.12	386.02	75.99	394.21	97.33	400.32	116.08	406.03	136.08	411.13	156.12
377.39	57.66	386.59	77.35	394.70	98.64	400.73	117.42	406.36	137.30	411.46	157.43
377.92	58.68	387.13	78.65	395.17	99.94	401.13	118.75	406.75	138.76	411.77	158.77
378.60	60.00	387.69	80.00	395.56	101.32	401.52	120.09	407.11	140.09	412.05	159.89
379.29	61.37	388.23	81.33	396.06	102.67	401.93	121.43	407.45	141.43		
379.96	62.66	388.75	82.67	396.46	103.91	402.32	122.76	407.79	142.70		
380.63	64.02	389.29	84.01	396.90	105.26	402.69	124.06	408.15	144.08		
Propyl Butanoate											
388.10	42.68	399.41	61.34	407.10	77.31	413.58	93.35	418.17	106.65	425.57	130.65
390.05	45.39	400.78	63.98	408.28	80.01	414.45	95.95	419.48	110.65	426.68	134.65
391.67	48.02	402.14	66.64	409.39	82.64	415.43	98.65	420.82	114.65	427.78	138.65
393.38	50.69	403.43	69.31	410.42	85.39	415.94	99.99	422.00	118.65	428.50	141.32
394.98	53.34	404.67	71.97	411.44	87.93	416.57	101.32	423.24	122.65	429.20	143.98
396.50	56.01	405.90	74.66	412.48	90.59	416.85	102.65	424.41	126.65	429.90	146.65
398.01	58.73										

Table 5. Coefficients *A*, *B*, and *C* and Standard Deviations $s(p_i^\circ)$ Obtained for the Antoine Equation, $\log(p_i^\circ/\mathrm{kPa}) = A - B/[T/(\mathrm{K}) - C]$, and Those from the Literature

compound	*A*	*B*	*C*	$s(p_i^\circ)$/kPa	range, *T*/*K*	ref
propyl methanoate	6.07030	1181.20	63.30	0.05	320−375	this work
	5.97008	1132.30	68.35		260−380	TRC (1993)
	6.16037	1226.68	58.39		290−360	Fárková and Wichterle (1993)
propyl ethanoate	6.51160	1524.56	36.19	0.09	320−430	this work
	6.05546	1233.46	70.07		280−400	TRC (1993)
	6.07167	1240.55	69.10		325−400	Fárková and Wichterle (1993)
	6.17309	1294.40	64.15		280−410	Reid et al. (1987)
propyl propanoate	6.06539	1301.06	75.11	0.04	360−420	this work
	6.44890	1545.30	47.85		300−420	TRC (1993)
	6.19565	1383.66	65.07		330−395	Fárková and Wichterle (1993)
	6.01127	1276.62	76.08		375−405	Ortega and Galván (1994)
propyl butanoate	6.60941	1723.42	42.02	0.08	375−440	this work
	5.40455	1019.49	116.55		300−460	TRC (1993)
	6.32482	1543.16	59.45		345−430	Fárková and Wichterle (1993)
	5.97273	1331.41	80.07		375−450	Ortega and Galván (1995)
propan-2-ol	6.87294	1365.38	70.04	0.05	330−370	this work
	7.24268	1580.92	53.54		275−375	TRC (1993)
	6.86618	1360.13	75.56			Riddick et al. (1986)
butan-2-ol	6.44632	1218.04	97.96	0.08	350−390	this work
	6.59921	1314.19	86.60		290−400	TRC (1993)
	6.35457	1171.89	103.20			Riddick et al. (1986)

differed substantially from the most recent values in the literature (Fárková and Wichterle, 1993), new measurements for those components were taken in the present study. Table 5 gives the values for the coefficients of the Antoine equation calculated by a method of nonlinear regression together with literature values for purposes of comparison. The differences found between published curves calculated using the Antoine equation and those reported here for the same temperature interval have been graphically represented in Figure 2 together with the ±1% curves. The largest discrepancies were for the propyl esters as temperature increased, with mean differences in pressure of up to 3% with respect to the correlations for propyl propanoate and propyl butanoate published in previous papers (Ortega and Galván 1994, 1995). As in other papers, the correlations of the (T, p_i°) pairs were performed using the corresponding reduced quantities. Figure 3 gives plots of the vapor pressures for each of the propyl esters and alkan-2-ols used in this study, with a vertical line drawn at $T_r = 0.7$, which according to Pitzer (1955) is appropriate for analytical and graphic determination of the acentric factors ω for use in subsequent calculations. These values are given in Table 1 together with literature values, with which they displayed good agreement.

Presentation and Reduction of VLE Data

Table 6 presents the isobaric VLE data for the eight mixtures empirically written as $\{x_1C_{u-1}H_{2u+1}COOC_3H_7$ $(u = 1-4) + x_2CH_3CH(OH)CH_3$ or $+ x_2CH_3CH(OH)CH_2CH_3\}$ employed in this study at the different equilibrium states. Table 6 gives the most characteristic VLE variables, T, x_1, and y_1, along with the values of such indirectly calculated ones as γ_1, γ_2, and G_m^E/RT.

In the calculations, the vapor phase was regarded as nonideal, and the activity coefficients were determined using

$$\gamma_i = [\phi_i p y_i/(p_i^\circ x_i \phi_i^\circ)] \exp[(p_i^\circ - p)V_i^\circ/RT] \qquad (2)$$

where V_i° was the molar volume of pure component i, calculated for each equilibrium temperature using a modified version of Rackett's equation [see Spencer and Danner (1972)]. The values of the parameter Z_{RA} used for propyl methanoate, propyl ethanoate, and propan-2-ol were the literature values published by Spencer and Danner (1972) and Reid et al. (1987). For the other components, the values for that parameter were calculated using $V_i^\circ = f(T)$ with the values published by TRC (1990). The fugacity coefficients ϕ_i and ϕ_i° in eq 3 were calculated using

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

where B_{ij} are the second virial coefficients for the pure components and the mixtures in the truncated virial equation as calculated using the correlation of Tsonopoulos (1974). Figures 4 gives plots of the activity coefficients and the Gibbs dimensionless function, G_m^E/RT against propyl ester concentration. The plots show maximum and minimum activity coefficient (γ_i) values and the corresponding inflection in the Gibbs function at low alkanol concentrations. This increases with the molecular weight of the ester (propanoate and butanoate) in the mixture, revealing interactions with the higher molecular weight esters due to the larger structural differences in the molecules. This effect decreases the probable exothermic component in the mixing enthalpy, which may be larger for the methanoates and the ethanoates, though in all cases the final or net H_m^E values were positive (Ortega and Plácido, 1995). Maximum and minimum γ_i values were not observed for the mixtures containing propyl methanoate and propyl ethanoate. This is due to endothermic effects caused by rupture of the hydrogen bonds and weakening of the polar forces in the alkanols and in these two propyl esters, since in these cases the molecular sizes are similar.

The point-to-point test proposed by Fredenslund et al. (1977) was applied to the eight mixtures considered here, and the results were consistent as defined by that method. The influence of the enthalpic term was negligible in all cases.

No isobaric VLE values for these mixtures have been located in the literature for comparison. The literature has yielded only isothermal values for the mixture consisting of propyl ethanoate + butan-2-ol at $T = 313$ K published by Shakhud et al. (1972), as reported by Gmehling et al. (1977, Vol. I, part 2f, p 225).

Azeotropes. Azeotropes were observed in four of the systems studied at the working pressure 101.32 kPa, namely, in the mixtures composed of propyl methanoate (1) + propan-2-ol (2) at $x_1 = 0.570$ and $T = 349.4$ K, propyl

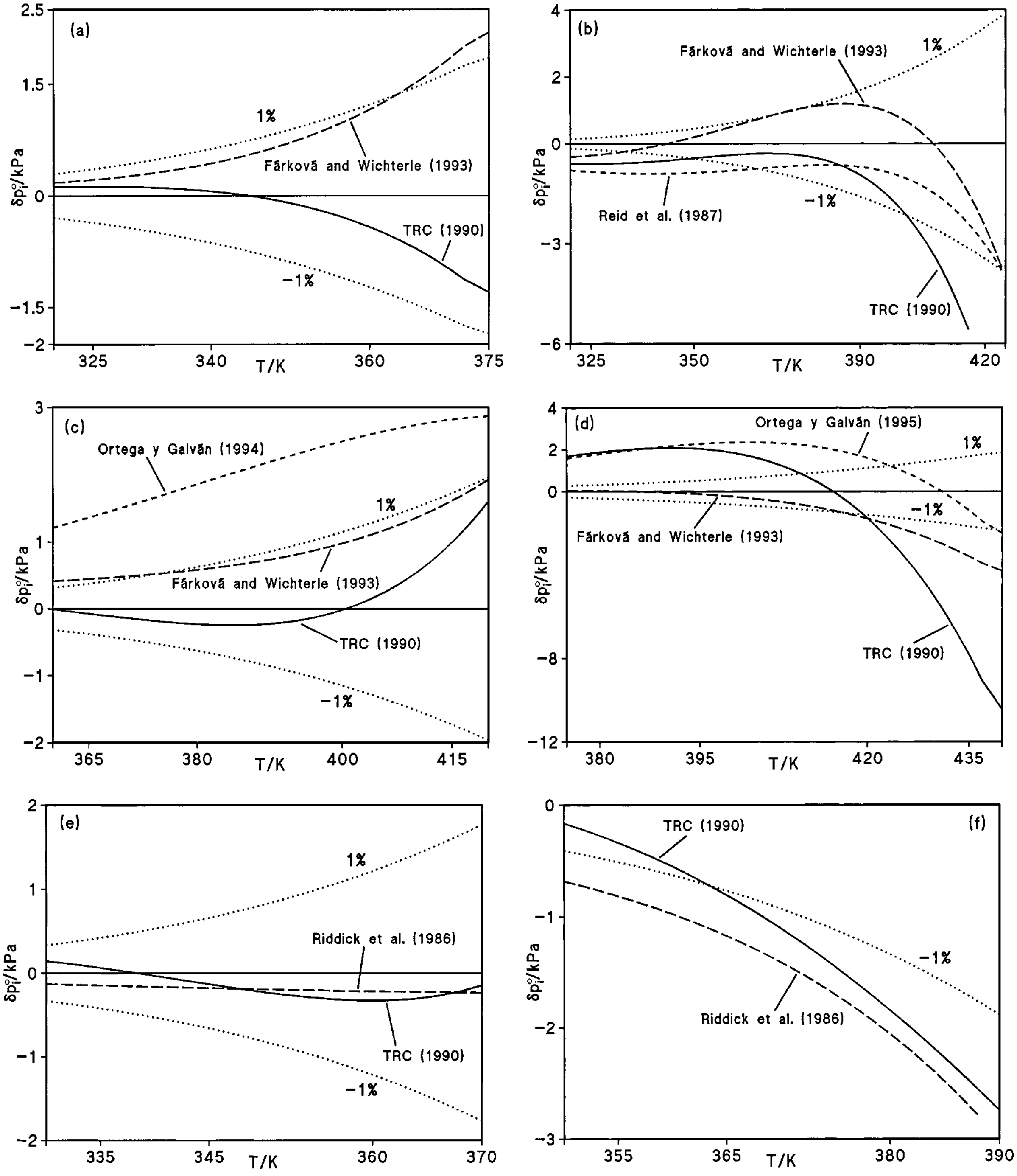

Figure 2. Differences, $\delta p_i^\circ/\text{kPa} = p_{i,\text{lit}}^\circ - p_{i,\text{exp}}^\circ$ of vapor pressures between the values calculated using the parameters from the literature and ours from Table 5 employing the Antoine equation for the pure compounds used in this work: (a) propyl methanoate; (b) propyl ethanoate; (c) propyl propanoate; (d) propyl butanoate; (e) propan-2-ol; (f) butan-2-ol.

methanoate (1) + butan-2-ol (2) at $x_1 = 0.933$ and $T = 353.6$ K, propyl ethanoate (1) + propan-2-ol (2) at $x_1 = 0.037$ and $T = 355.2$ K, and propyl ethanoate (1) + butan-2-ol (2) at $x_1 = 0.423$ and $T = 370.8$ K. The specialized literature (Gmehling et al., 1994) contains values for two of the above four mixtures at the same working pressure, namely, an azeotrope for propyl methanoate (1) + propan-2-ol (2) at $x_1 = 0.548$ and $T = 349.1$ K, which is close to that obtained by us, and an azeotrope for propyl ethanoate (1) + butan-2-ol (2) at $x_1 = 0.392$ and $T = 370.5$ K, which is at a difference of 0.03 units in ester mole fraction. In the isothermal values published by Shakhud et al. (1972) [given in Gmehling et al. (1977, Vol. 1, part 2f, p 225), the estimated values for this same mixture were $x_1 = 0.805$ and $T = 313$ K ($p = 10.4$ kPa). All these values, except that obtained by Shakhud et al. (1972), have been plotted using the corresponding reduced coordinates in Figure 3 together with the vapor pressure curves for the pure components and the azeotropic line for the mixture propyl ethanoate + butan-2-ol, which was obtained in this case using the azeotrope presented by Shakhud et al. (1972). The mixing rules used for the critical magnitudes were the geometric means corresponding to the individual values for the components making up the mixture considered, that is, $p_{cij} = (p_{ci}p_{cj})^{1/2}$ and $T_{cij} = (T_{ci}T_{cj})^{1/2}$. In that way the azeotropic line intersected with the vertical line at $T_r = 0.7$, yielding a theoretical value of 0.434 for the acentric factor for the set of all the mixtures contributing to the

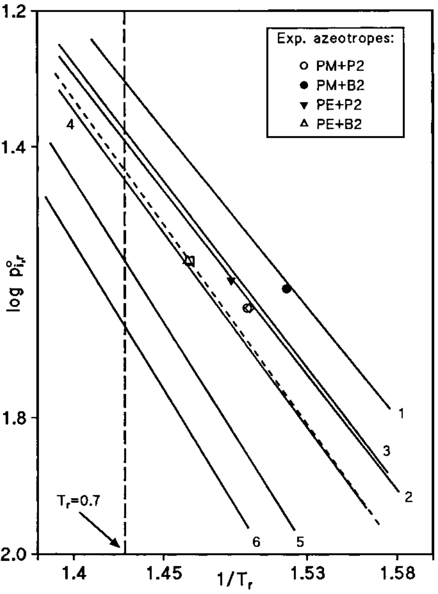

Figure 3. Experimental vapor pressure lines obtained with the values from Table 4 plotted in reduced coordinates for pure compounds [(1) propyl methanoate, log $p_{i,r}^\circ = -3.278/T_r + 3.380$; (2) propyl ethanoate, log $p_{i,r}^\circ = -3.404/T_r + 3.472$; (3) propyl propanoate, log $p_{i,r}^\circ = -3.450/T_r + 3.553$; (4) propyl butanoate, log $p_{i,r}^\circ = -3.601/T_r + 3.696$; (5) butan-2-ol, log $p_{i,r}^\circ = -4.197/T_r + 4.427$; (6) propan-2-ol, log $p_{i,r}^\circ = -4.319/T_r + 4.506$] and the azeotropic line (- - -) for propyl ethanaote + butan-2-ol. Azeotropes from the literature: (◇) for propyl methanoate + propan-2-ol and (□) for propyl ethanoate + butan-2-ol, both from Gmehling et al. (1994).

azeotropic line. This is very close to the arithmetic mean of the ω_i values for the components of the mixture propyl ethanoate (1) + butan-2-ol (2), i.e., that is, since, bearing in mind the definition of the acentric factor given by Pitzer (1955), for binary mixtures we have

$$\omega = \frac{\omega_1 + \omega_2}{2} = \frac{1}{2}[(-\log p_{1,r}^\circ - 1) + (-\log p_{2,r}^\circ - 1)] = -\log p_{i,r}^\circ - 1 \quad (4)$$

where

$$p_r^\circ = \sqrt{p_{1,r}^\circ\, p_{2,r}^\circ} = p/\sqrt{p_{1,c}^\circ\, p_{2,c}^\circ} \quad (5)$$

Correlation of VLE Data. The isobaric VLE data for all the propyl ester (1) + alkan-2-ol (2) mixtures were reduced by applying the correlation equation proposed in an earlier paper by Soto et al. (1998), using the Solver computational subroutine from Excel from Microsof spreadsheet version 5.0a. The basis of the model is the correlation of the dimensionless form of the Gibbs function $Q = G_m^E/RT$ with the ester mole fraction x_l using eq 1 with temperature-dependent coefficients. This allows the equation to be written

$$Q = x_1x_2\left[\left(\frac{A_{01}}{T} + A_{02}\right) + \left(\frac{A_{11}}{T} + A_{12}\right)z + \left(\frac{A_{21}}{T} + A_{22}\right)z^2 + ...\right] \quad (6)$$

where z is defined as in eq 2. The coefficients in eq 7 can then be related to the corresponding coefficients in the enthalpy correlation using an equation similar to eq 1. For proper identification, the excess enthalpies should be transformed to their dimensionless form for fitting as in

$$H_m^E/RT = x_1x_2\sum A_i^1 z^i \quad (7)$$

and a relation for the coefficients in eqs 7 and 8 can then readily be derived taking into account the thermodynamic expression $H_m^E = [\partial(G_m^E/T)/\partial(1/T)]_{px}$, yielding $A_i^1 = A_{i1}/T$. Thus, two procedures may be used to calculate the coefficients in eq 7: (1) by determining the values of A_{i1} through correlation of excess enthalpies using eq 8 and then holding those values constant and calculating the values of A_{i2} using the VLE data, G_m^E/RT, and γ_i or (2) by calculating all the coefficients can be calculated together in one procedure using a single objective function. This latter method was also used to correlate the VLE quantities with the commonly employed Wilson, NRTL, and UNIQUAC local composition equations.

The excess enthalpies for the mixtures considered in this study were determined at our laboratory earlier by Ortega and Plácido (1995). Table 7 presents the results of the correlations for the dimensionless forms of the enthalpies using eq 8. The objective function defined as

$$OF = \sum_i^N\left[\sum_{j=1}^2\frac{(X_{i,\mathrm{cal}} - X_{i,\mathrm{exp}})^2}{0.05^2} + \frac{(Y_{i,\mathrm{cal}} - Y_{i,\mathrm{exp}})^2}{0.01^2} + \frac{(Z_{i,\mathrm{cal}} - Z_{i,\mathrm{exp}})^2}{0.1^2}\right] \quad (8)$$

where $X = \gamma_j$, $Y = G_m^E/RT$, and $Z = H_m^E/RT$, was used to correlate the dimensionless Gibbs energies, excess enthalpies, and activity coefficients. The above-mentioned equations derived from the local composition models did not produce good mixing enthalpies. The mixing enthalpies had rather high mean errors in most cases which were in excess of 50% for many of the mixtures using the Wilson and NRTL equations. The UNIQUAC model yielded more acceptable results, with a mean error of less than 15% for the eight mixtures considered. However, the best results were achieved using the equation proposed here. Table 8 gives the results for the fits obtained using eqs 2 and 7; the largest difference was smaller than 2%, for the mixture propyl methanoate (1) + butan-2-ol (2). For the remaining seven mixtures, the mean difference was around 1%. The top portion of Figure 5 compares the equimolar values of H_m^E recorded experimentally and the estimates of those same values obtained using the correlations for the eight mixtures considered; the agreement is good.

Prediction of the VLE Values

Previous work has demonstrated the usefulness of various group-contribution models for isobaric equilibria of mixtures of propyl esters with normal and isomeric alkanols. The models used to estimate the VLE values were the original UNIFAC model, that of Fredenslund et al. (1975), that revised by Hansen et al. (1991), the modified-UNIFAC model published by Gmehling et al. (1993), and the ASOG model by Tochigi et al. (1990).

The ASOG model yielded excellent predictions for the mixtures containing propyl methanoate, with differences of 3% for the activity coefficients. For the other binary mixtures, the discrepancies increased progressively with the chain length of the ester and alkanol components, ranging from 5% for propyl ethanoate + propan-2-ol to 9% for propyl butanoate + butan-2-ol. The model yielded fairly good predictions for the location of the azeotropes for those

Table 6. VLE Experimental Values, $T-x_1-y_1$, and Calculated Values Obtained at 101.32 kPa for Binary Systems of Propyl Esters (1) + Alkan-2-ol (2)

T/K	x_1	y_1	γ_1	γ_2	G^E_m/RT	T/K	x_1	y_1	γ_1	γ_2	G^E_m/RT
Propyl Methanoate (1) + Propan-2-ol (2)											
355.30	0.000	0.000		1.000	0.000	349.41	0.543	0.554	1.174	1.231	0.182
354.96	0.008	0.021	2.590	1.002	0.009	349.41	0.558	0.563	1.160	1.248	0.181
354.68	0.017	0.041	2.355	1.001	0.015	349.42	0.594	0.586	1.135	1.285	0.177
354.57	0.021	0.049	2.293	1.000	0.018	349.43	0.598	0.587	1.130	1.292	0.176
354.24	0.033	0.073	2.182	1.000	0.026	349.53	0.635	0.616	1.112	1.320	0.169
353.47	0.064	0.126	1.996	1.003	0.048	349.68	0.670	0.641	1.091	1.358	0.159
352.80	0.094	0.172	1.898	1.008	0.067	349.78	0.692	0.658	1.080	1.382	0.153
352.16	0.129	0.222	1.808	1.011	0.086	349.88	0.708	0.670	1.073	1.397	0.148
351.55	0.167	0.265	1.708	1.022	0.108	349.99	0.727	0.685	1.065	1.420	0.141
351.00	0.209	0.308	1.609	1.036	0.128	350.20	0.759	0.710	1.051	1.467	0.130
350.64	0.245	0.342	1.542	1.047	0.141	350.35	0.779	0.724	1.038	1.518	0.121
350.35	0.275	0.368	1.493	1.059	0.152	350.65	0.811	0.754	1.028	1.564	0.107
350.08	0.315	0.398	1.423	1.079	0.163	351.00	0.846	0.789	1.020	1.626	0.092
349.91	0.346	0.421	1.380	1.093	0.170	351.53	0.889	0.834	1.009	1.739	0.069
349.87	0.352	0.426	1.373	1.097	0.171	351.89	0.915	0.864	1.005	1.821	0.056
349.83	0.355	0.428	1.371	1.099	0.173	352.05	0.925	0.876	1.003	1.876	0.050
349.80	0.362	0.433	1.360	1.103	0.174	352.21	0.935	0.890	1.003	1.906	0.045
349.79	0.368	0.438	1.353	1.104	0.174	352.40	0.944	0.902	1.000	1.984	0.038
349.66	0.398	0.458	1.313	1.124	0.179	352.59	0.951	0.913	0.999	1.998	0.033
349.56	0.430	0.480	1.277	1.145	0.182	352.60	0.955	0.918	1.000	2.044	0.032
349.47	0.461	0.501	1.247	1.166	0.184	352.85	0.966	0.934	1.000	2.098	0.025
349.43	0.489	0.519	1.219	1.187	0.185	353.12	0.976	0.950	0.997	2.249	0.017
349.41	0.518	0.537	1.194	1.210	0.184	353.75	1.000	1.000	1.000		0.000
Propyl Ethanoate (1) + Propan-2-ol (2)											
355.30	0.000	0.000		1.000	0.000	357.95	0.441	0.307	1.162	1.122	0.130
355.20	0.005	0.007	2.593	1.003	0.008	358.43	0.471	0.331	1.151	1.126	0.129
355.20	0.009	0.011	2.202	1.004	0.011	358.86	0.504	0.350	1.124	1.146	0.127
355.20	0.014	0.016	2.062	1.004	0.014	359.33	0.555	0.370	1.063	1.217	0.121
355.20	0.019	0.021	1.945	1.004	0.017	359.80	0.572	0.390	1.069	1.206	0.118
355.21	0.025	0.026	1.908	1.004	0.020	360.27	0.602	0.409	1.049	1.235	0.113
355.23	0.036	0.037	1.850	1.004	0.026	360.75	0.623	0.427	1.043	1.241	0.108
355.25	0.049	0.048	1.782	1.005	0.033	361.28	0.652	0.448	1.029	1.269	0.102
355.30	0.072	0.069	1.728	1.005	0.044	361.81	0.670	0.469	1.030	1.264	0.097
355.40	0.107	0.096	1.633	1.009	0.061	361.81	0.672	0.467	1.022	1.277	0.095
355.46	0.124	0.109	1.599	1.012	0.068	362.43	0.696	0.489	1.013	1.292	0.087
355.60	0.160	0.137	1.532	1.018	0.083	363.45	0.730	0.524	1.003	1.306	0.074
355.66	0.165	0.140	1.525	1.017	0.084	364.30	0.755	0.556	1.003	1.300	0.067
355.80	0.192	0.159	1.484	1.022	0.093	365.87	0.811	0.623	0.996	1.353	0.054
355.79	0.198	0.163	1.470	1.026	0.097	366.62	0.836	0.658	0.997	1.380	0.050
356.00	0.219	0.178	1.448	1.025	0.100	367.47	0.857	0.691	0.996	1.381	0.043
356.16	0.253	0.195	1.357	1.045	0.110	368.00	0.868	0.713	0.997	1.375	0.040
356.40	0.281	0.214	1.331	1.051	0.116	369.16	0.895	0.760	0.996	1.378	0.031
356.86	0.340	0.247	1.251	1.077	0.125	371.76	0.951	0.877	1.000	1.402	0.016
357.14	0.374	0.263	1.204	1.099	0.128	374.31	1.000	1.000	1.000		0.000
357.55	0.410	0.287	1.178	1.113	0.130						
Propyl Propanoate (1) + Propan-2-ol (2)											
353.30	0.000	0.000		1.000	0.000	357.14	0.136	0.070	1.728	1.006	0.080
355.32	0.005	0.006	4.053	1.000	0.007	357.53	0.162	0.078	1.607	1.012	0.087
355.33	0.005	0.006	4.127	1.000	0.007	358.19	0.206	0.097	1.530	1.021	0.105
355.33	0.005	0.006	4.057	1.000	0.007	358.81	0.249	0.113	1.445	1.036	0.118
355.33	0.006	0.006	3.853	1.000	0.008	359.37	0.283	0.131	1.442	1.042	0.133
355.33	0.007	0.007	3.574	1.001	0.009	360.68	0.361	0.161	1.333	1.074	0.149
355.34	0.007	0.007	3.568	1.000	0.009	361.90	0.419	0.188	1.279	1.094	0.155
355.35	0.007	0.007	3.470	1.000	0.009	363.30	0.490	0.217	1.205	1.142	0.159
355.35	0.007	0.007	3.406	1.000	0.009	364.76	0.547	0.245	1.158	1.178	0.154
355.35	0.015	0.015	3.532	1.000	0.019	366.92	0.619	0.282	1.095	1.232	0.136
355.57	0.016	0.012	2.670	0.995	0.011	371.06	0.719	0.357	1.041	1.297	0.102
355.61	0.026	0.021	2.794	0.996	0.023	373.80	0.765	0.415	1.039	1.288	0.088
355.76	0.032	0.020	2.236	0.996	0.022	380.05	0.856	0.561	1.031	1.285	0.063
355.82	0.045	0.030	2.354	0.997	0.036	387.43	0.933	0.752	1.016	1.244	0.030
356.19	0.074	0.044	2.076	0.999	0.053	390.95	0.965	0.859	1.014	1.226	0.020
356.58	0.104	0.058	1.915	1.003	0.071	392.00	0.972	0.888	1.010	1.179	0.015
356.68	0.109	0.056	1.771	1.007	0.068	395.56	1.000	1.000	1.000		0.000
356.87	0.113	0.059	1.780	1.001	0.066						
Propyl Butanoate (1) + Propan-2-ol (2)											
355.30	0.000	0.000		1.000	0.000	368.68	0.539	0.136	1.115	1.151	0.124
355.81	0.019	0.005	2.003	0.996	0.009	369.83	0.578	0.148	1.080	1.194	0.119
356.14	0.035	0.010	1.926	0.996	0.019	371.70	0.620	0.168	1.072	1.213	0.116
356.47	0.052	0.014	1.884	0.996	0.029	374.23	0.662	0.194	1.060	1.217	0.105
356.93	0.075	0.020	1.804	0.998	0.042	376.91	0.707	0.221	1.034	1.240	0.086
357.94	0.125	0.032	1.672	1.003	0.067	384.45	0.804	0.319	1.021	1.276	0.065
358.78	0.166	0.041	1.579	1.010	0.084	387.65	0.832	0.361	1.005	1.269	0.044
359.74	0.212	0.052	1.489	1.020	0.100	393.55	0.873	0.455	1.004	1.205	0.027
360.68	0.260	0.063	1.422	1.037	0.118	396.45	0.897	0.508	1.000	1.229	0.021
361.73	0.305	0.073	1.349	1.051	0.126	401.90	0.927	0.620	1.003	1.153	0.013
363.00	0.354	0.084	1.276	1.067	0.128	407.70	0.957	0.747	0.991	1.125	−0.004
364.30	0.403	0.095	1.212	1.089	0.128	411.60	0.976	0.842	0.982	1.130	−0.015
365.78	0.455	0.110	1.180	1.113	0.134	415.30	0.993	0.952	0.987	1.047	−0.013
367.15	0.499	0.122	1.133	1.137	0.127	416.57	1.000	1.000	1.000		0.000
367.34	0.502	0.124	1.137	1.135	0.127						

Table 6. (Continued)

T/K	x_1	y_1	γ_1	γ_2	G^{E}_{m}/RT	T/K	x_1	y_1	γ_1	γ_2	G^{E}_{m}/RT
Propyl Methanoate (1) + Butan-2-ol (2)											
372.27	0.000	0.000		1.000	0.000	360.18	0.387	0.579	1.240	1.080	0.130
371.59	0.018	0.052	1.741	0.989	−0.001	360.25	0.389	0.577	1.227	1.085	0.130
370.74	0.036	0.095	1.627	0.991	0.009	359.69	0.413	0.599	1.220	1.095	0.135
369.75	0.060	0.150	1.583	0.990	0.018	359.00	0.451	0.629	1.197	1.113	0.140
368.33	0.092	0.216	1.545	0.996	0.036	358.49	0.485	0.652	1.171	1.136	0.142
367.15	0.126	0.274	1.479	1.000	0.050	357.93	0.523	0.676	1.145	1.167	0.145
365.77	0.167	0.336	1.422	1.011	0.068	357.44	0.558	0.699	1.126	1.194	0.144
364.65	0.205	0.389	1.384	1.017	0.080	356.93	0.610	0.723	1.082	1.271	0.141
364.15	0.224	0.408	1.347	1.028	0.089	356.45	0.635	0.747	1.089	1.264	0.140
363.76	0.235	0.426	1.356	1.027	0.092	356.03	0.681	0.770	1.060	1.338	0.133
363.56	0.244	0.436	1.344	1.029	0.094	355.55	0.735	0.795	1.029	1.464	0.122
363.28	0.258	0.449	1.319	1.035	0.097	355.10	0.766	0.822	1.035	1.466	0.116
362.85	0.268	0.464	1.329	1.038	0.103	354.73	0.801	0.848	1.032	1.495	0.106
362.74	0.276	0.472	1.317	1.038	0.103	354.31	0.851	0.880	1.021	1.604	0.088
362.38	0.288	0.485	1.310	1.044	0.108	353.96	0.886	0.903	1.017	1.719	0.077
361.85	0.311	0.508	1.290	1.052	0.114	353.75	0.917	0.922	1.010	1.906	0.063
361.93	0.312	0.506	1.278	1.054	0.113	353.58	0.947	0.944	1.007	2.169	0.047
361.33	0.335	0.531	1.271	1.060	0.119	353.68	0.969	0.962	1.000	2.507	0.028
361.05	0.350	0.543	1.254	1.068	0.122	353.75	1.000	1.000	1.000		0.000
360.75	0.363	0.555	1.247	1.074	0.125						
Propyl Ethanoate (1) + Butan-2-ol (2)											
372.27	0.000	0.000		1.000	0.000	370.75	0.442	0.438	1.111	1.062	0.080
371.98	0.017	0.027	1.678	1.000	0.009	370.77	0.471	0.463	1.098	1.072	0.081
371.88	0.033	0.047	1.552	0.999	0.013	370.80	0.477	0.469	1.100	1.069	0.080
371.62	0.067	0.086	1.413	1.002	0.025	370.84	0.505	0.492	1.087	1.080	0.081
371.42	0.099	0.123	1.358	1.004	0.034	370.88	0.538	0.520	1.077	1.093	0.081
371.25	0.134	0.160	1.322	1.005	0.042	370.96	0.574	0.550	1.066	1.106	0.080
371.14	0.169	0.196	1.282	1.008	0.048	371.10	0.611	0.582	1.054	1.121	0.077
371.01	0.202	0.229	1.259	1.011	0.055	371.26	0.654	0.622	1.047	1.135	0.074
370.92	0.235	0.260	1.231	1.015	0.061	371.48	0.697	0.662	1.040	1.147	0.069
370.85	0.268	0.291	1.209	1.020	0.065	371.72	0.742	0.704	1.031	1.172	0.063
370.79	0.300	0.319	1.188	1.026	0.070	371.96	0.780	0.741	1.026	1.189	0.058
370.78	0.330	0.346	1.172	1.030	0.072	372.26	0.821	0.782	1.018	1.219	0.051
370.77	0.361	0.370	1.146	1.040	0.075	372.64	0.865	0.831	1.015	1.238	0.042
370.76	0.363	0.373	1.151	1.038	0.075	373.05	0.908	0.881	1.012	1.271	0.033
370.76	0.395	0.402	1.137	1.044	0.077	373.55	0.955	0.937	1.009	1.356	0.022
370.76	0.414	0.415	1.121	1.054	0.078	374.31	1.000	1.000	1.000		0.000
370.75	0.423	0.424	1.122	1.054	0.079						
Propyl Propanoate (1) + Butan-2-ol (2)											
372.27	0.000	0.000		1.000	0.000	377.85	0.449	0.300	1.124	1.047	0.078
372.56	0.024	0.021	1.745	0.992	0.006	378.30	0.474	0.317	1.110	1.053	0.077
372.67	0.037	0.030	1.600	0.993	0.011	378.85	0.499	0.336	1.102	1.053	0.074
372.88	0.058	0.044	1.502	0.993	0.017	379.50	0.533	0.360	1.080	1.068	0.072
373.20	0.087	0.064	1.428	0.992	0.024	380.18	0.577	0.383	1.041	1.109	0.067
373.53	0.117	0.084	1.377	0.993	0.031	380.74	0.597	0.402	1.038	1.108	0.064
373.81	0.148	0.103	1.335	0.996	0.040	381.49	0.624	0.431	1.042	1.101	0.062
374.14	0.176	0.121	1.305	0.998	0.045	382.25	0.649	0.460	1.042	1.094	0.058
374.50	0.204	0.140	1.285	0.998	0.050	383.90	0.712	0.524	1.030	1.113	0.052
374.83	0.232	0.158	1.262	1.001	0.055	384.90	0.747	0.563	1.025	1.123	0.048
375.15	0.254	0.172	1.247	1.002	0.057	386.10	0.782	0.610	1.023	1.121	0.043
375.29	0.278	0.186	1.224	1.013	0.066	387.45	0.820	0.663	1.019	1.126	0.037
375.75	0.307	0.204	1.197	1.016	0.066	390.48	0.893	0.781	1.009	1.121	0.021
376.02	0.334	0.220	1.177	1.026	0.072	392.72	0.946	0.879	1.006	1.146	0.014
376.45	0.363	0.239	1.161	1.032	0.074	394.12	0.974	0.939	1.005	1.136	0.008
376.75	0.386	0.256	1.158	1.036	0.078	395.56	1.000	1.000	1.000		0.000
377.38	0.426	0.281	1.127	1.048	0.078						
Propyl Butanoate (1) + Butan-2-ol (2)											
372.27	0.000	0.000		1.000	0.000	383.16	0.477	0.199	1.116	1.056	0.081
372.37	0.005	0.003	2.058	0.999	0.002	384.12	0.508	0.215	1.096	1.067	0.079
372.71	0.025	0.010	1.605	0.999	0.010	385.32	0.540	0.236	1.091	1.067	0.077
373.36	0.060	0.024	1.487	0.999	0.023	386.40	0.570	0.255	1.077	1.076	0.074
374.06	0.099	0.038	1.414	1.001	0.035	387.62	0.601	0.276	1.065	1.083	0.070
374.94	0.147	0.056	1.337	1.007	0.049	388.37	0.619	0.290	1.061	1.085	0.068
375.66	0.182	0.069	1.309	1.010	0.057	390.18	0.657	0.324	1.056	1.086	0.064
376.50	0.224	0.085	1.266	1.016	0.065	392.34	0.702	0.365	1.040	1.098	0.056
377.45	0.267	0.100	1.219	1.024	0.070	394.40	0.738	0.408	1.037	1.094	0.051
378.33	0.306	0.117	1.201	1.030	0.077	397.12	0.781	0.464	1.027	1.093	0.040
379.50	0.351	0.135	1.169	1.036	0.077	400.45	0.828	0.540	1.021	1.086	0.031
380.10	0.371	0.146	1.169	1.035	0.079	404.04	0.874	0.629	1.014	1.082	0.022
380.45	0.387	0.152	1.149	1.043	0.079	407.61	0.915	0.726	1.009	1.076	0.015
380.85	0.401	0.158	1.143	1.044	0.080	411.08	0.950	0.824	1.002	1.061	0.005
381.21	0.418	0.164	1.122	1.055	0.079	413.79	0.975	0.907	0.998	1.048	−0.001
381.55	0.424	0.171	1.137	1.046	0.081	416.57	1.000	1.000	1.000		0.000
382.27	0.451	0.183	1.123	1.054	0.081						

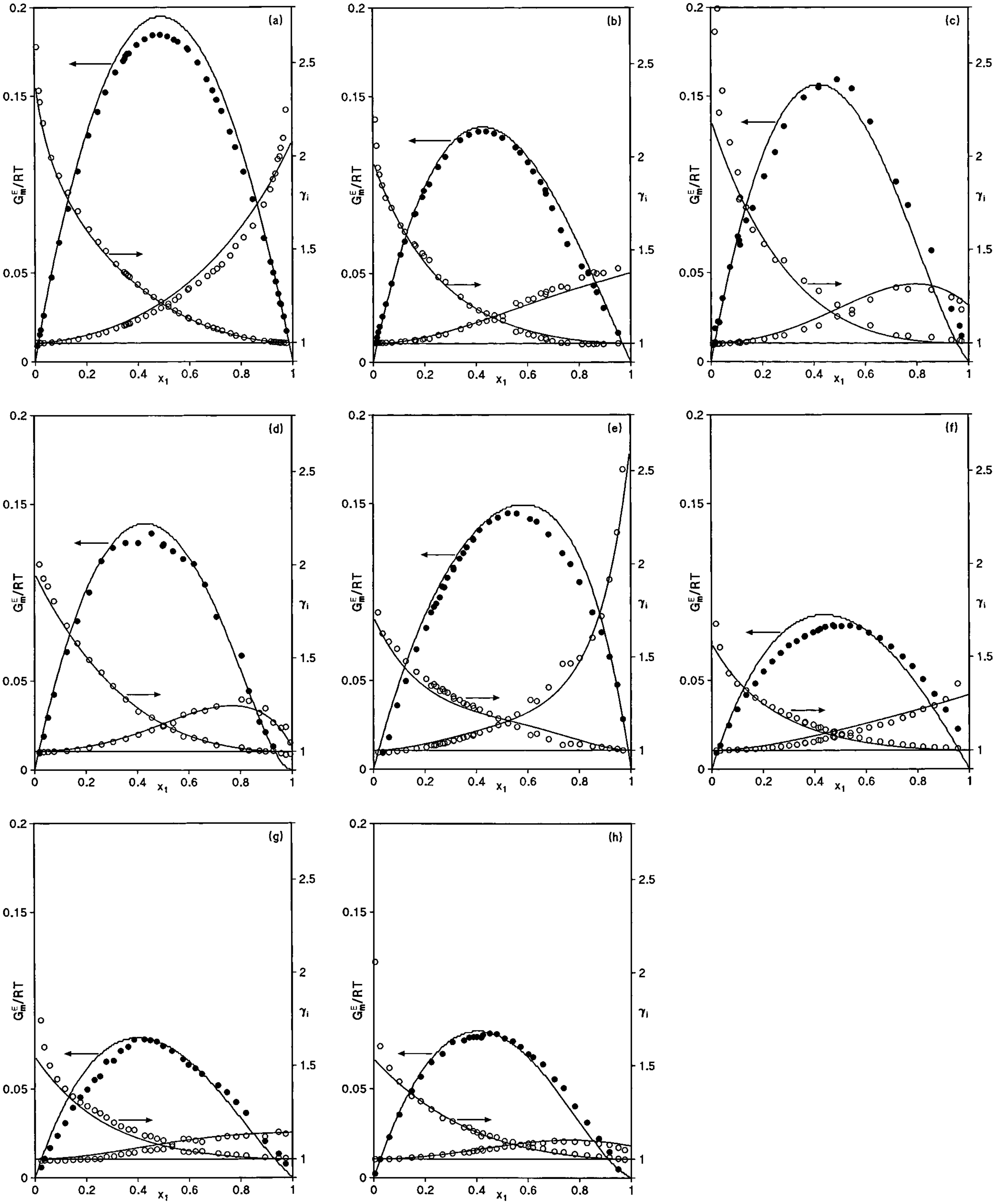

Figure 4. Experimental values and correlation curves using eq 7 corresponding to G_m^E/RT (●) and γ_i (○) obtained for the following mixtures: (a) propyl methanoate + propan-2-ol; (b) propyl ethanoate + propan-2-ol; (c) propyl propanoate + propan-2-ol; (d) propyl butanoate + propan-2-ol; (e) propyl methanoate + butan-2-ol; (f) propyl ethanoate + butan-2-ol; (g) propyl propanoate + butan-2-ol; (h) propyl butanoate + butan-2-ol.

mixtures presenting singular points, except the case of the system propyl methanoate + butan-2-ol, which, according to the model, did not present an azeotrope.

The original version of the UNIFAC model using the parameters published by Hansen et al. (1991) did not yield good estimates of the activity coefficients, and the differences increased progressively with the chain length of the mixture components, reaching as high as 23%. Though the model did predict all the azeotropes found in this study, the coordinates predicted presented discrepan-

Table 7. Coefficients of Eq 8 Obtained in Correlation of Experimental Excess Molar Enthalpies in the Form $Z = H_m^E/RT$ versus x_1, for Propyl Esters (1) + Alkan-2-ol (2) at 298.15 K

mixture	k	A_0^1	A_0^1	$s(Z)$
propan-2-ol(2) +				
propyl methanoate (1)	7.21	2.736	0.471	0.086
propyl ethanoate (1)	0.84	2.951	−0.295	0.064
propyl propanoate (1)	2.17	2.731	−0.023	0.073
propyl butanoate (1)	0.41	2.591	0.114	0.072
butan-2-ol (2) +				
propyl methanoate (1)	1.21	3.249	−0.308	0.062
propyl ethanoate (1)	9.71	3.074	−0.549	0.074
propyl propanoate (1)	0.34	2.959	−0.025	0.029
propyl butanoate (1)	0.21	2.834	0.077	0.049

Table 8. Fitting Coefficients for Eq 7 Obtained Correlating the Quantities $Y = G_m^E/RT$, $Z = H_m^E/RT$, and γ_i versus x_1 and Standard Deviations $s(\gamma_i)$, $s(Y)$, and $s(Z)$ for Binary Mixtures of Propyl Esters (1) + Alkan-2-ol (2)

	coefficients		$s(\gamma_i)$	$s(Y)$	$s(Z)$
	Propyl Methanoate (1) + Propan-2-ol (2)				
$k = 0.75^a$	$A_{01} = 815.9$	$A_{11} = 140.4$	0.078	0.010	0.01
	$A_{02} = -1.528$	$A_{12} = -0.452$			
	Propyl Ethanoate (1) + Propan-2-ol (2)				
$k = 0.41^a$	$A_{01} = 879.8$	$A_{11} = -88.1$	0.012	0.006	0.01
	$A_{02} = -1.756$	$A_{12} = 0.000$			
	Propyl Propanoate (1) + Propan-2-ol (2)				
$k = 2.60^a$	$A_{01} = 814.3$	$A_{11} = -6.9$	0.047	0.0107	0.01
	$A_{02} = -1.522$	$A_{12} = -0.392$			
	Propyl Butanoate (1) + Propan-2-ol (2)				
$k = 2.43^a$	$A_{01} = 772.5$	$A_{11} = 33.9$	0.020	0.007	0.01
	$A_{02} = -1.476$	$A_{12} = -0.392$			
	Propyl Methanoate (1) + Butan-2-ol (2)				
$k = 4.08^a$	$A_{01} = 968.9$	$A_{11} = -91.9$	0.044	0.012	0.02
	$A_{02} = -2.163$	$A_{12} = 0.709$			
	Propyl Ethanoate (1) + Butan-2-ol (2)				
$k = 9.77^a$	$A_{01} = 916.5$	$A_{11} = -163.9$	0.043	0.005	0.01
	$A_{02} = -2.123$	$A_{12} = 0.434$			
	Propyl Propanoate (1) + Butan-2-ol (2)				
$k = 0.24^a$	$A_{01} = 882.2$	$A_{11} = -7.4$	0.037	0.006	0.01
	$A_{02} = -1.881$	$A_{12} = -0.172$			
	Propyl Butanoate (1) + Butan-2-ol (2)				
$k = 1.29^a$	$A_{01} = 845.0$	$A_{11} = 23.1$	0.016	0.004	0.01
	$A_{02} = -1.833$	$A_{12} = -0.184$			

[a] Obtained by fit; $s(F) = [\sum_{i=1}^{N}(F_{i,\text{exp}} - F_{i,\text{cal}})^2/N]^{1/2}$; N, number of experimental points.

cies linked to the differences in the estimates of γ_i.

The version of the UNIFAC model published by Gmehling et al. (1993) yielded the best estimates of the activity coefficients for the set of all the mixtures considered in the study. The largest difference was 6% for the mixture propyl propanoate + propan-2-ol. On the negative side, the model failed to estimate an azeotrope for the system propyl ethanoate + propan-2-ol; though the literature does not contain values for that singular point, it was predicted by the other models employed in this work. The estimates of the excess enthalpies for these same systems using this modified version of the UNIFAC model with the same set of parameter values as those for the VLE data yielded H_m^E values that were lower than the experimental values in all cases, with differences ranging from 13% for the mixtures containing ethanoate to 27% for the systems containing propyl propanoate and propyl butanoate + butan-2-ol. Equimolar values for H_m^E, obtained using this model, are presented in Figure 5 together with experimental values and those calculated from correlation of VLE data.

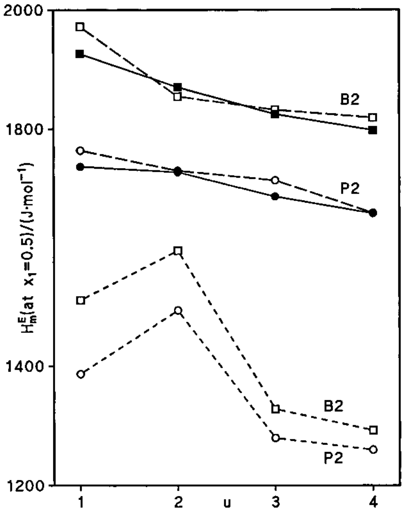

Figure 5. Plot of equimolar value excess enthalpies $H_m^E(x_1 = 0.5)$ for the mixtures propyl esters + propan-2-ol (P2) or + butan-2-ol (B2): (—) experimental values; (− − −) correlated values using eq 7; (- - -) estimated values using the UNIFAC model from Gmehling et al. (1993).

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