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Thermodynamic Study of Binary Mixtures Containing an Isobutylalkanol and an Alkyl (Ethyl to Butyl) Alkanoate (Methanoate to Butanoate), Contributing with Experimental Values of Excess Molar Enthalpies and Volumes, and Isobaric Vapor−Liquid Equilibria

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This paper reports measurements on vapor−liquid equilibria and other mixing thermodynamic properties, V_m^E and H_m^E, for 12 binary mixtures formed by 12 aliphatic esters (from methanoate to butanoate) and 2-methylpropan-1-ol. To complete the study another set of data published previously containing methyl alkanoates (ethanoate to butanoate) with the same isobutylalkanol is also incorporated into the interpretation of the behavior of these mixtures. All equilibrium data were found to be consistent using a version of a point-to-point test, and for the data correlation a new equation containing temperature-dependent parameters was used to relate the equilibrium quantities and excess enthalpies; the results were acceptable. To observe the regularity of results obtained, a matrix for the more relevant quantities for the vapor−liquid equilibrium is presented. For the set of 15 mixtures considered in this study, only five presented azeotropes, namely, isobutylalkanol + methyl butanoate, + ethyl propanoate, + propyl ethanoate, + propyl propanoate, and + butyl methanoate. The ASOG and modified-UNIFAC models estimate well the activity coefficients for the mixtures considered in this study; however, this last model, using the same set of interaction parameters, predicts fairly well the excess enthalpies of all mixtures with differences ranging from 12 to 26%.

Introduction

Previous papers dealing with mixtures of alkyl esters and alkanols published by our research group have presented new values and analyzed the thermodynamic behavior of that class of binary mixtures, particularly those containing the shortest-chain isomeric alkanols (C_3, C_4). Studies performed on 2-methylpropan-1-ol (isobutylalkanol) remain to be published. There are few literature values for the properties of mixtures of that component with alkyl esters. A brief review of studies on mixtures containing that butanol isomer found in the literature is discussed below.

Ortega and Susial (1995) published isobaric vapor−liquid equilibrium (VLE) values at 101.32 kPa for mixtures of isobutylalkanol and the shortest-chain methyl esters, and Susial and Ortega (1993, 1995) published the values for those same mixtures at other pressures. Linek (1979) reported the VLE values for isobutylalkanol + butyl methanoate also at 101.3 kPa, and Seselkin et al. (1985) also studied that same mixture. Finally, Volkova et al. (1979) [see Gmehling et al. (1977) Vol. I/2f, p 330], published the VLE values for isobutylalkanol + butyl butanoate at that same pressure. In Gmehling et al. (1994) important discrepancies in the azeotropic points published for mixtures of isobutylalkanol and various alkyl esters were observed. The new values presented in this paper for a set of 12 mixtures of isobutylalkanol and the first four ethyl, propyl, and butyl esters will help corroborate the goodness of the literature values and will at the same time contribute values not heretofore available in the literature.

The extant literature likewise contains few studies of the excess magnitudes for mixtures containing isobutylalkanol, even though they are so essential in describing the behavior of mixtures. Nikam et al. (1996) published the V_m^E values for isobutylalkanol + ethyl ethanoate, and a paper published by our group, Gonzalez et al. (1996), presented the V_m^E values for a mixture of isobutylalkanol and propyl esters. Excess enthalpies H_m^E had been published earlier by Ortega and Placido (1995), and the literature consulted only yielded enthalpic values for the binary mixtures consisting of isobutylalkanol and ethyl and butyl ethanoate [see Christensen et al. (1984), Vol. III, Part 1, pp 651 and 752]. For this work we also have measured the V_m^E and H_m^E values for systems not previously studied by our group, which will help contribute to existing knowledge of mixtures containing isomers.

Both the VLE and the values of the excess quantities will be appropriately correlated using an equation employed in earlier papers by our group, and several group-contribution models were also used to estimate the properties of the mixtures and test the applicability of those theoretical models to systems containing alkanol isomers. The literature studies on mixtures of isobutylalkanol + methyl esters referred to above were also used in this paper in order to present a more complete analysis of all the properties and a better understanding of the mixtures considered.

Experimental Section

Materials. The alkyl esters employed in the experimentation were the same as those in earlier works, and their

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Table 1. Experimental Excess Molar Volumes V_m^E at (298.15 ± 0.01) K for Binary Mixtures Isobutylalkanol (1) + Alkyl Esters (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}	x_1	ρ/kg·m^{-3}	$10^9 V_m^E$/m^3·mol^{-1}
Isobutylalkanol (1) + Ethyl Methanoate (2)											
0.0000	914.35	0	0.2551	877.98	335	0.5099	846.78	427	0.7984	816.22	289
0.0219	910.66	68	0.3238	869.18	376	0.5872	838.12	416	0.8929	807.24	180
0.1346	894.31	221	0.3845	861.63	405	0.6483	831.55	392	0.9685	800.38	72
0.1966	885.80	283	0.4484	853.94	422	0.7198	824.11	349	1.0000	797.87	0
Isobutylalkanol (1) + Ethyl Ethanoate (2)											
0.0000	894.34	0	0.2881	864.85	313	0.5504	839.20	382	0.8027	815.51	253
0.0809	885.91	111	0.3480	858.89	348	0.6193	832.67	363	0.8804	808.33	181
0.1603	877.74	205	0.4193	851.97	364	0.6735	827.56	339	0.9286	803.95	123
0.2259	871.03	273	0.4895	845.12	378	0.7399	821.38	296	1.0000	797.87	0
Isobutylalkanol (1) + Ethyl Propanoate (2)											
0.0000	883.93	0	0.3402	856.97	219	0.6049	834.65	218	0.8399	813.25	130
0.0727	878.29	72	0.3841	853.38	227	0.6627	829.50	209	0.8962	807.92	90
0.1732	870.37	150	0.4609	846.93	241	0.7223	824.08	194	1.0000	797.87	0
0.2463	864.57	186	0.5359	840.58	236	0.7808	818.77	162			
Isobutylalkanol (1) + Ethyl Butanoate (2)											
0.0000	873.94	0	0.3392	852.03	222	0.6103	832.36	219	0.8441	812.76	117
0.0756	869.05	68	0.4095	847.23	228	0.6739	827.27	205	0.8989	807.64	90
0.1655	863.39	145	0.4806	842.12	236	0.7344	822.24	186	0.9682	800.97	37
0.2534	857.84	179	0.5522	836.79	234	0.7907	817.43	156	1.0000	797.87	0
Isobutylalkanol (1) + Propyl Methanoate (2)											
0.0000	899.31	0	0.2871	869.20	231	0.5435	842.97	288	0.7923	818.10	200
0.1471	883.81	136	0.3543	862.27	259	0.6168	835.55	281	0.8546	811.96	155
0.2123	876.91	192	0.4130	856.30	270	0.6668	830.56	264	0.8669	810.86	132
0.2197	876.19	193	0.4783	849.66	277	0.6700	830.26	260	1.0000	797.87	0
0.2815	869.81	224				0.7292	824.29	243			
Isobutylalkanol (1) + Propyl Ethanoate (2)											
0.0000	882.60	0	0.2749	860.99	236	0.4970	842.87	283	0.8112	815.53	174
0.0697	877.19	79	0.2956	859.38	240	0.5851	835.45	271	0.8528	811.67	151
0.1692	869.44	163	0.3423	855.58	262	0.6560	829.36	249	0.9137	806.04	97
0.2178	865.53	205	0.4875	843.65	286	0.7164	823.99	232	1.0000	797.87	0
Isobutylalkanol (1) + Propyl Propanoate (2)											
0.0000	875.59	0	0.4031	849.15	208	0.6207	832.59	200	0.8953	808.33	87
0.1094	868.79	96	0.4665	844.53	213	0.6776	827.93	183	0.9413	803.95	42
0.1994	863.07	144	0.5279	839.92	209	0.7360	822.93	166	1.0000	797.87	0
0.2757	857.95	184	0.5588	837.53	206	0.7948	817.75	138			
0.3491	852.97	198				0.8500	812.66	112			
Isobutylalkanol (1) + Propyl Butanoate (2)											
0.0000	867.95	0	0.3737	847.77	196	0.6446	829.60	179	0.9051	807.54	67
0.0954	863.17	82	0.4480	843.14	206	0.6985	825.49	162	0.9500	803.13	36
0.1997	857.69	144	0.5236	838.18	203	0.7590	820.56	145	1.0000	797.87	0
0.2170	856.81	142	0.5803	834.30	190	0.8154	815.79	114			
0.2965	852.28	185				0.8596	811.83	91			
Isobutylalkanol (1) + Butyl Methanoate (2)											
0.0000	888.10	0	0.3187	861.69	214	0.5838	838.11	255	0.7650	821.32	162
0.0889	880.89	86	0.3898	855.42	250	0.5856	837.94	256	0.8354	814.43	128
0.1896	872.69	142	0.3912	855.33	247	0.6589	831.27	226	0.8984	808.21	80
0.2515	867.37	191	0.4922	846.39	261	0.7058	826.88	208	1.0000	797.87	0
Isobutylalkanol (1) + Butyl Ethanoate (2)											
0.0000	876.12	0	0.2184	862.04	186	0.5587	837.53	249	0.8413	813.46	140
0.0890	870.54	86	0.2848	857.60	211	0.6082	833.58	243	0.9084	807.07	94
0.1210	868.54	105	0.3743	851.32	241	0.7208	824.15	213	1.0000	797.87	0
0.2134	862.40	179	0.4406	846.47	256	0.7852	818.52	179			
Isobutylalkanol (1) + Butyl Propanoate (2)											
0.0000	870.83	0	0.3787	849.68	177	0.5574	837.59	175	0.8493	813.52	76
0.0823	866.61	63	0.4399	845.71	179	0.5581	837.55	176	0.8672	811.77	69
0.1290	864.22	89	0.4512	844.95	181	0.5901	835.22	168	0.8982	808.74	54
0.2100	859.80	122	0.4934	842.12	181	0.7114	825.69	137	1.0000	797.87	0
0.3100	853.93	162	0.5089	841.02	181	0.8199	816.22	93			
Isobutylalkanol (1) + Butyl Butanoate (2)											
0.0000	864.39	0	0.2140	854.80	150	0.4960	839.53	203	0.7770	819.57	124
0.0850	860.68	84	0.2890	851.06	184	0.5360	837.09	198	0.8610	812.17	80
0.1530	857.64	128	0.3900	845.78	199	0.6070	832.49	178	0.9660	801.82	15
0.1890	855.94	147	0.4240	843.82	203	0.6120	832.09	175	1.0000	797.87	0
0.2090	855.04	150	0.4670	841.36	204	0.6540	829.12	165			

physical properties were not very different from already published values (Ortega and Susial, 1995; Ortega and Plácido, 1995; Hernandez and Ortega, 1997; Soto et al., 1998). The isobutylalkanol employed was from Fluka, puriss p.a. >99.5 mass %, and before use both it and the alkyl esters were degassed for several hours and then dried

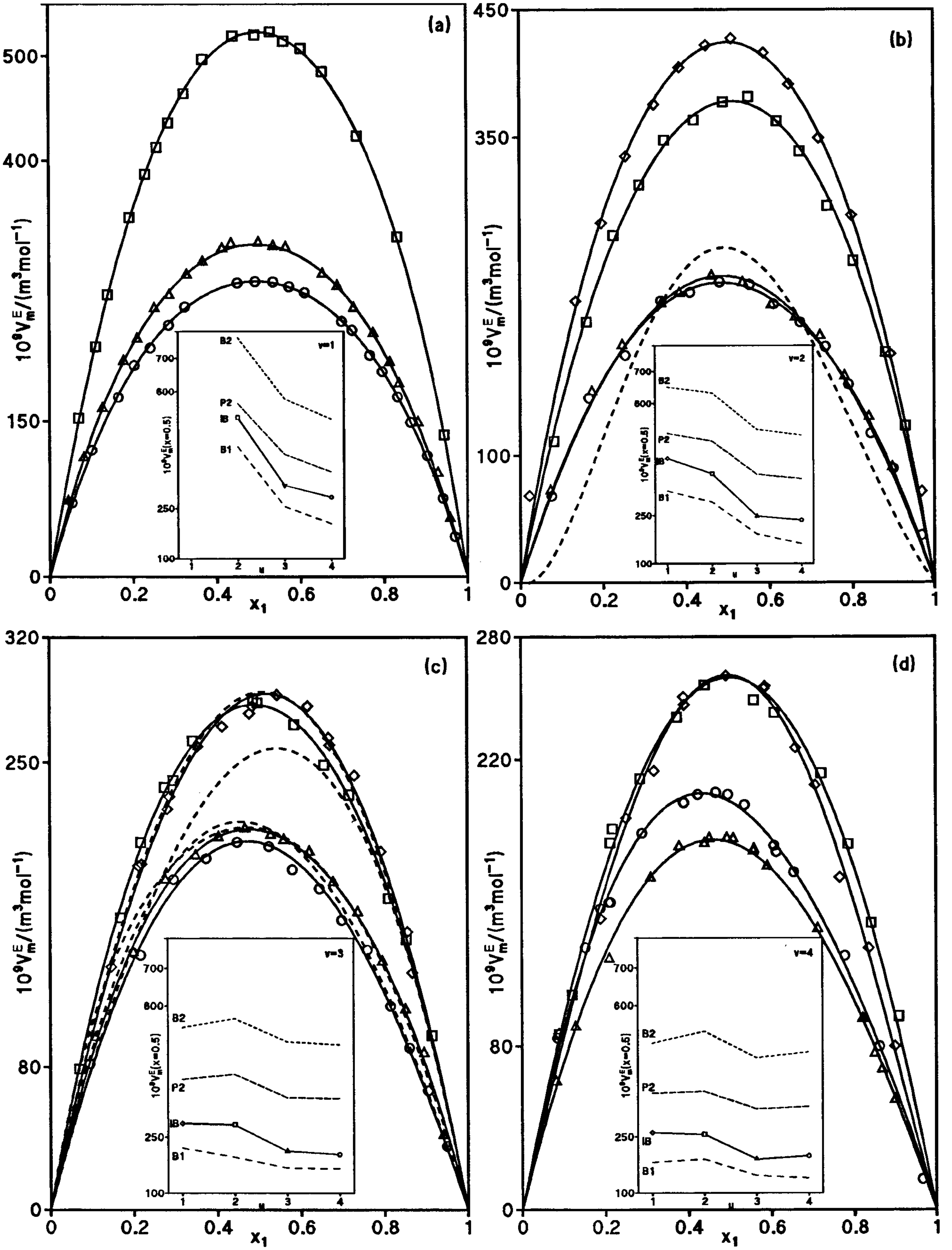

Figure 1. Experimental values and correlation curves of V_m^E versus x_1 for binary mixtures isobutylalkanol (1) + alkyl esters (2): (a) isobutylalkanol (IB) + methyl ethanoate (□), + methyl propanoate (△), + methyl butanoate (○); (b) isobutylalkanol (IB) + ethyl methanoate (◇), + ethyl ethanoate (□), + ethyl propanoate (△) + ethyl butanoate (○), and (- - -) Nikam et al. (1996); (c) isobutylalkanol (IB) + propyl methanoate (◇), + propyl ethanoate (□), + propyl propanoate (△), + propyl butanoate (○), and (- - -) González et al. (1996); (d) isobutylalkanol (IB) + butyl methanoate (◇), + butyl ethanoate (□), + butyl propanoate (△), + butyl butanoate (○). Inset figures show the variation of equimolar volumes for binary mixtures formed by $C_{u-1}H_{2u-1}COOC_vH_{2v+1}$ + isobutylalkanol (IB), + butan-2-ol (B2), + propan-2-ol (P2), and + butan-1-ol (B1).

Table 2. Experimental Excess Molar Enthalpies H^{E}_{m} Obtained at (298.15 ± 0.01) K for Binary Mixtures Isobutylalkanol (1) + Alkyl Esters (2)

x_1	H^{E}_{m}/J·mol $^{-1}$	x_1	H^{E}_{m}/J·mol $^{-1}$	x_1	H^{E}_{m}/J·mol $^{-1}$	x_1	H^{E}_{m}/J·mol $^{-1}$	x_1	H^{E}_{m}/J·mol $^{-1}$	x_1	H^{E}_{m}/J·mol $^{-1}$
Isobutylalkanol (1) + Ethyl Methanoate (2)											
0.0459	426.6	0.2466	1684.4	0.3994	2024.4	0.5253	2027.9	0.6757	1706.2	0.9393	500.7
0.0974	866.1	0.3002	1852.9	0.4416	2051.7	0.5666	1965.3	0.7439	1494.7		
0.1519	1225.5	0.3504	1957.1	0.4853	2058.9	0.6183	1854.4	0.8124	1207.8		
0.2032	1486.4	0.3994	2024.4	0.5153	2030.9			0.8748	883.2		
Isobutylalkanol (1) + Ethyl Ethanoate (2)											
0.0581	451.8	0.2463	1440.0	0.4252	1847.9	0.5845	1799.5	0.7572	1321.8	0.9445	377.5
0.1210	851.4	0.3114	1651.2	0.4755	1881.3	0.6382	1694.1	0.8201	1047.1		
0.1867	1193.9	0.3711	1772.1	0.5211	1875.6	0.6958	1537.9	0.8836	719.7		
Isobutylalkanol (1) + Ethyl Propanoate (2)											
0.0677	512.2	0.2761	1504.1	0.4563	1766.3	0.5209	1755.1	0.6423	1587.4	0.8223	984.4
0.1406	925.7	0.3466	1676.8	0.4699	1776.9	0.5400	1745.3	0.6995	1437.2	0.8874	668.5
0.2146	1266.5	0.4106	1754.4	0.4970	1771.3	0.5893	1680.6	0.7583	1239.8	0.9520	323.5
Isobutylalkanol (1) + Ethyl Butanoate (2)											
0.0774	583.3	0.2989	1487.2	0.5023	1703.2	0.6236	1561.7	0.7853	1122.3	0.9581	280.9
0.1448	934.6	0.3748	1636.0	0.5548	1669.1	0.6740	1460.3	0.8436	878.7		
0.2163	1239.6	0.4428	1700.3	0.5753	1636.4	0.7286	1314.1	0.9021	589.0		
Isobutylalkanol (1) + Butyl Methanoate (2)											
0.0653	516.7	0.2810	1532.7	0.4655	1803.7	0.5787	1711.2	0.7329	1375.0	0.9012	638.2
0.1361	937.6	0.3464	1687.7	0.4981	1760.1	0.6276	1639.1	0.7892	1172.0	0.9528	337.3
0.2108	1287.8	0.4079	1766.9	0.5335	1752.9	0.6798	1526.8	0.8454	926.6		
Isobutylalkanol (1) + Butyl Ethanoate (2)											
0.0779	542.2	0.3154	1519.1	0.5039	1732.0	0.6134	1628.9	0.7596	1247.9	0.9141	532.9
0.1591	952.6	0.3853	1655.4	0.5290	1727.7	0.6603	1539.9	0.8120	1017.0	0.9599	272.8
0.2397	1291.6	0.4477	1719.3	0.5699	1686.5	0.7097	1406.3	0.8637	790.2		
Isobutylalkanol (1) + Butyl Propanoate (2)											
0.0542	326.1	0.2345	1146.4	0.3426	1452.9	0.4519	1641.8	0.5742	1638.0	0.8151	1074.0
0.1147	641.7	0.2900	1327.0	0.3898	1559.0	0.5090	1664.0	0.6468	1549.5	0.9048	652.3
0.1749	913.4			0.4042	1585.4			0.7264	1368.8		
Isobutylalkanol (1) + Butyl Butanoate (2)											
0.0752	560.9	0.2819	1461.7	0.4441	1687.9	0.6034	1575.4	0.7332	1284.7	0.8769	710.8
0.1487	951.1	0.3408	1587.2	0.4890	1688.9	0.6442	1505.4	0.7806	1126.8	0.9232	464.5
0.2189	1261.2	0.3954	1658.8	0.5289	1666.4	0.6883	1409.0	0.8284	935.1	0.9675	212.2

over molecular sieves (Fluka, 0.3 nm). Then the purity of the isobutylalkanol was checked with a GC model HP-6890 equipped with a FID, and any significant impurities were observed to be practically coincident with those shown by supplier. The experimental values obtained for the physical properties were as follows: n(D,298.15 K) = 1.3935, 1.3939 (Riddick et al., 1986; TRC, a-5030 1967); at 298.15 K, ρ/(k·gm^{-3}) = 797.87, 797.80 (Riddick et al., 1986; TRC, a-5030 1967); $T^{\circ}_{b,1}$ = 380.95 K, 380.81 (Riddick et al., 1986), 380.90 (Linek, 1979).

Equipment and Procedure. The experimental system used to determine the VLE values was described by Ortega and Susial (1991), though some auxiliary equipment was modified. Specifically, temperature was measured using a Comarks Electronic Ltd. model 6800 digital thermometer equipped with PT100 sensor periodically calibrated using another ASL-F25 thermometer/calibrator according to standard ITS-90. The estimated precision of the readings was ±0.02 K. Pressure in the experiments was measured and regulated using a Desgranges et Hout model PPC2 controller/calibration unit, stabilizing the pressure readings at (101.32 ± 0.02) kPa. The compositions of the equilibrium phases were determined indirectly using some correlations $\rho = \rho(x)$ obtained previously for each of the mixtures by preparing samples of known concentration and measuring the density at a constant temperature of (298.15 ± 0.01) K in an Anton Paar model DMA-55 digital densimeter to a precision of ±0.02 kg·m^{-3}. Simple polynomial correlations were then used to calculate the concentrations of each of the equilibrium phases, the precision of the calculations being estimated at better than ±0.002 units. Validation of the experimental densities for the mixtures was carried out by verifying the results for V^{E}_{m}.

Mixing enthalpies were determined directly, also at temperature of (298.15 ± 0.01) K using a Calvet-type Setaram model MS80D microcalorimeter calibrated electrically, and the quality of the readings was verfied using known mixtures such as cyclohexane + hexane from McGlashan and Stoeckli (1969) and benzene + heptadecane from Diaz-Peña and Menduiña (1974). The uncertainty in the experimental results was estimated at less than 1% of the H^{E}_{m} values.

Results and Discussion

Densities and Excess Volumes. Density measurements for the mixtures comprising isobutylalkanol (1) + an alkyl ester (2), obtained using the densimeter mentioned above, were performed for a set of concentrations for each of the mixtures. The corresponding excess volumes V^{E}_{m} were then calculated from the density measurements to a precision of ±10^{-4} units for the mole fraction and ±2 × 10^{-9} m^{3}·mol^{-1} for the V^{E}_{m} values. The results are presented in Table 1, and all the values were correlated using an equation of the type

$$10^{9}V^{E}_{m}/(\mathrm{m^{3}\cdot mol^{-1}}) = x_1x_2\sum b_i z^{i} \text{ where } z = x_1/(x_1 + k_v x_2) \tag{1}$$

where the value of $k_v = V^{\circ}_{2}/V^{\circ}_{1}$ was the quotient of the molar volumes of the pure components at the working temperature, as proposed by Ortega and Alcalde (1992),

Table 3. Molar Volumes V_i° for Pure Compounds at 298.15 K and Fitting Coefficients for V_m^E and H_m^E versus x_1 of Isobutylalkanol (1) + Alkyl Esters (2) Using Eq 1

binary mixture	$10^6V_i^\circ$/m^3·mol^{-1}	$k_v = V_2^\circ/V_1^\circ$	b_0	b_1	b_2	$10^9s(V_m^E)$/m^3·mol^{-1}
isobutylalkanol (1) +	92.91[a]					
methyl ethanoate (2)	79.91[a]	0.860	2486	−1608	1630	4
methyl propanoate (2)	96.89[a]	1.043	1581	−1155	1090	3
methyl butanoate (2)	114.47[a]	1.232	1390	−1052	1088	2
ethyl methanoate (2)	81.02[a]	0.872	2013	−1194	1130	3
ethyl ethanoate (2)	98.52[a]	1.060	1628	−592	728	6
ethyl propanoate (2)	115.54[a]	1.244	1009	−103		5
ethyl butanoate (2)	132.95[a]	1.431	1049	−403	348	5
propyl methanoate (2)	97.97[a]	1.055	1067	172		5
propyl ethanoate (2)	115.72[a]	1.246	1271	−554	523	4
propyl propanoate (2)	132.67[a]	1.428	999	−578	520	4
propyl butanoate (2)	149.99[a]	1.614	899	−202		4
butyl methanoate (2)	115.00[a]	1.238	867	835	−977	6
butyl ethanoate (2)	132.58[a]	1.427	1035	12		5
butyl propanoate (2)	149.48[a]	1.609	816	−251		2
butyl butanoate (2)	166.84[a]	1.796	1024	−775	408	4

$Q^h = H_m^E/RT$

binary mixture	k	A_0^1	A_1^1	A_2^1	$s(Q^h)$
isobutylalkanol (1) +					
methyl ethanoate (2)	5.06[b]	3.595	−0.256		0.004
methyl propanoate (2)	0.21[b]	3.787	−0.727		0.003
methyl butanoate (2)	0.21[b]	3.660	−0.784		0.005
ethyl methanoate (2)	0.22	4.450	−1.390		0.010
ethyl ethanoate (2)	1.02	3.264	−0.488		0.003
ethyl propanoate (2)	0.59	3.233	−0.591		0.004
ethyl butanoate (2)	0.13	3.595	−0.955		0.004
propyl methanoate (2)	0.16[c]	4.011	−2.351	1.290	0.003
propyl ethanoate (2)	1.42[c]	2.833	−0.059		0.004
propyl propanoate (2)	1.65[c]	2.861	−0.375		0.003
propyl butanoate (2)	0.93[c]	2.844	−0.315		0.004
butyl methanoate (2)	0.13	3.799	−1.016		0.008
butyl ethanoate (2)	0.84	2.917	−0.223		0.004
butyl propanoate (2)	0.22	3.236	−0.685		0.003
butyl butanoate (2)	0.18	3.493	−0.897		0.005

[a] Calculated using the densities. [b] Ortega and Plácido (1996). [c] Ortega and Plácido (1995).

and was held constant for each of the mixtures. The coefficients b_i were determined using a linear-regression procedure in which the degree of the polynomial was optimized to achieve the smallest standard deviation $s(V_m^E)$. The coefficients for each binary system are given in Table 3. Figure 1 plots the experimental points and the fitted curves for the mixtures considered in this study for each type of ester (methyl to butyl) employed and compares the results with existing literature values for those same systems.

The curve obtained for the mixture isobutylalkanol + ethyl ethanoate in this study displayed a marked discrepancy of more than 50% with respect to that published by Nikam et al. (1996) [see Figure 1b] due to large differences at the extreme concentrations, ascribable to the less precise pycnometric method employed by the authors of that earlier study. The V_m^E values for the mixtures composed of isobutylalkanol and the propyl esters, re-determined in this study to obtain the needed VLE values, were compared with other values published previously by Gonzalez et al. (1996). The differences with respect to those values were minimal except for the system consisting of isobutylalkanol + propyl ethanoate, which exhibited mean discrepancies of around 12% along the central portion of the curve.

The boxes inset in the figures show the variations in the equimolar quantities $V_m^E(x{=}0.5)$ with ester chain length and display a gradual decline very similar to that for other butanol isomers, the values being lower than those for alkan-2-ol and higher than those for butan-1-ol, also represented. The changes in the V_m^E values with the alkanol followed the sequence secondary > primary and branched chain >straight chain. The figures also reveal an atypical variation pattern for the methanoates possibly attributable to the occurrence of intermolecular clumping causing a larger than expected decrease in the V_m^E values. Even so, the V_m^E values were positive in all cases.

Excess Molar Enthalpies. Table 2 shows the values of the excess molar enthalpies for those binary mixtures of isobutylalkanol (1) + an alkyl ester (2) for which no literature values were found. The experimental data pairs, alkanol concentration x_1, and excess enthalpy in adimensional form $Q^h = H_m^E/RT$ were correlated using an equation similar to eq 1 altered slightly for use in processing the VLE data (see eq 6 below), and the coefficients for all the mixtures are set out in Table 3. In this case the values of the parameter k were obtained by iteration, minimizing the standard deviation of the values $s(H_m^E/RT)$ to achieve the best fit. Figure 2 plots the experimental points and the fitted curves obtained for each system together with the curves compiled from the literature for comparison. The curve for the mixture consisting of isobutylalkanol + ethyl ethanoate obtained in this study differed only slightly (2%) from that published by Hirobe et al. (1926) [see Christensen et al. (1984), Vol. III/I, p 651], but the curve for the mixture consisting of isobutylalkanol + butyl ethanoate presented a larger discrepancy (9%) from that published by Kehlen and Fuhrmann (1978) [see Christensen et al. (1984), Vol. I/I, p 752]. The inset boxes show the variations in the equimolar enthalpies $H_m^E(x{=}0.5)$ with alkyl ester chain length, revealing a regular decrease as the alkyl portion

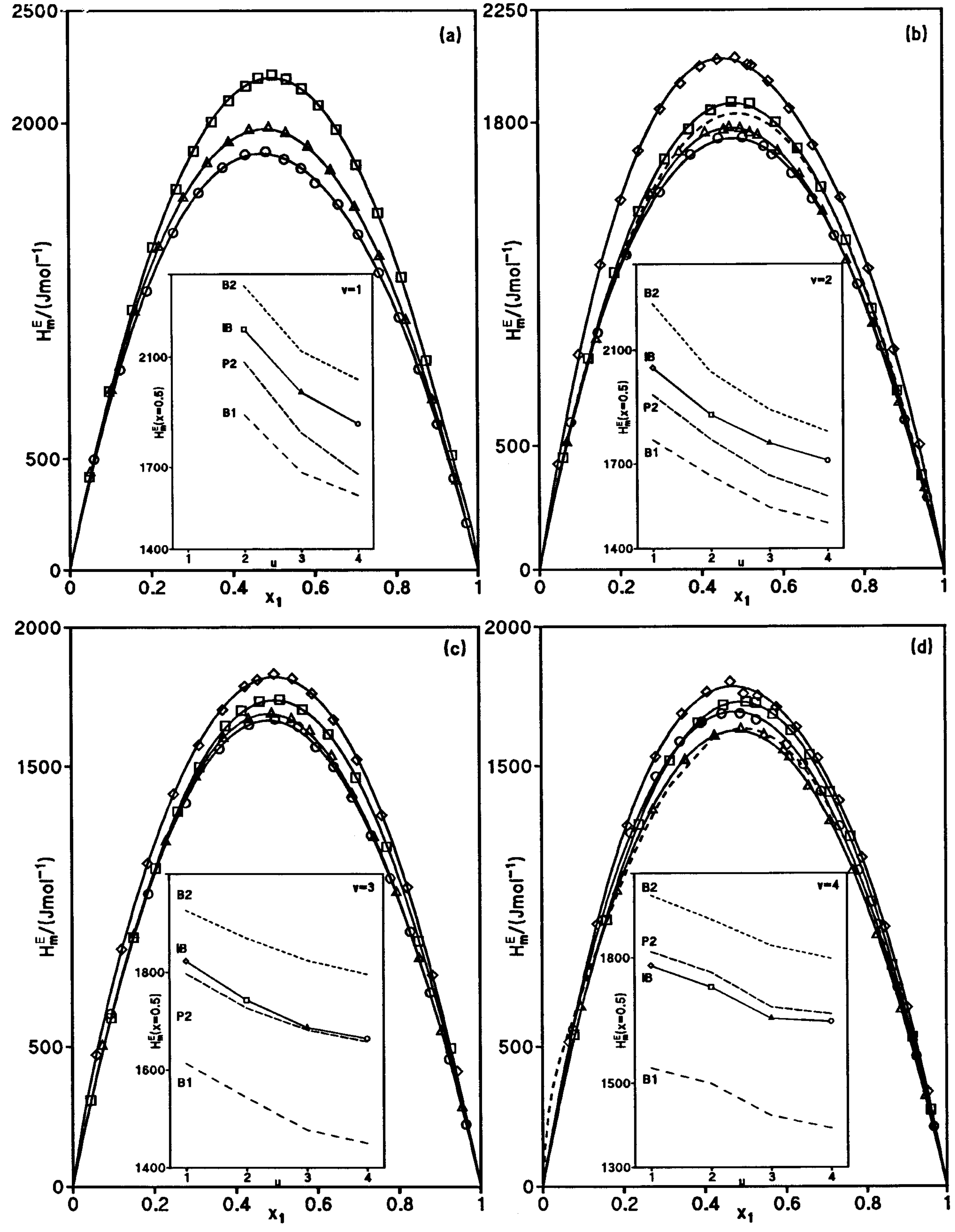

Figure 2. Experimental values and correlation curves of H_m^E versus x_1 for binary mixtures isobutylalkanol (1) + alkyl esters (2): (a) isobutylalkanol (IB) + methyl ethanoate (□), + methyl propanoate (△), + methyl butanoate (○); (b) isobutylalkanol (IB) + ethyl methanoate (◇), + ethyl ethanoate (□), + ethyl propanoate (△), + ethyl butanoate (○), and (- - -) Hirobe et al. (1926) [see Christensen et al. (1984), Vol. III/1, p 651]; (c) isobutylalkanol (IB) + propyl methanoate (◇), + propyl ethanoate (□), + propyl propanoate (△), + propyl butanoate (○), (d) isobutylalkanol (IB) + butyl methanoate (◇), + butyl ethanoate (□), + butyl propanoate (△), + butyl butanoate (○), and (- - -) Kehlen and Fuhrmann (1978) [see Christensen et al. (1984), Vol. III/1, p 752]. Inset figures show the variation of equimolar enthalpies for binary mixtures formed by $C_{u-1}H_{2u-1}COOC_vH_{2v+1}$ + isobutylalkanol (IB), + butan-2-ol (B2), + propan-2-ol (P2), and + butan-1-ol (B1).

Table 4. Experimental Vapor Pressures, T and p_i°, for Pure Isobutylalkanol

T/K	p_i°/kPa	T/K	p_i°/kPa	T/K	p_i°/kPa
358.15	40.89	377.63	89.36	385.65	119.87
360.84	45.91	378.03	90.70	386.12	121.92
362.81	49.86	378.41	92.01	386.62	123.97
364.26	52.94	378.82	93.39	387.06	125.96
365.32	55.33	379.17	94.63	387.49	127.86
367.03	59.14	379.57	96.03	388.03	130.33
368.22	62.03	379.94	97.35	388.37	131.90
369.03	64.05	380.32	98.71	388.81	134.00
369.81	66.20	380.68	99.99	389.22	135.86
370.56	68.08	380.95	101.32	389.81	138.65
371.29	70.07	381.74	104.01	390.34	141.22
371.99	72.07	382.04	105.21	390.91	144.03
372.69	74.04	382.39	106.58	391.44	146.66
373.39	76.07	382.75	108.01	391.96	149.31
374.03	78.00	383.12	109.50	392.47	151.95
374.72	80.07	383.42	110.66	392.99	154.66
375.09	81.23	383.74	111.93	393.50	157.32
375.57	82.71	384.03	113.10	393.72	158.52
375.99	84.03	384.40	114.61	393.98	160.00
376.39	85.33	384.74	116.03	394.20	161.26
376.82	86.71	385.03	117.25	394.44	162.57
377.22	88.02	385.36	118.64	394.98	165.32

of the esters increased, attributable to a lower energy requirement as the number of methylene groups on the molecule rose, due to a weakening of polar forces. The figures do not display the same atypical pattern for the methanoates referred to above; perhaps this was because the negative energy effects of the methanoates vis-à-vis the isobutylalkanol were not as pronounced as those in the plots of the excess volumes because the branched alkanol permits better coupling between the molecules of the mixture components.

An apparent inversion in the $H_m^E(x_1{=}0.5)$ values for the mixtures containing propan-2-ol was noted as the alkylated portion of the ester increased (see Figure 2d), inverting the previously established order (Figure 2a−c), possibly due to greater structural differences in the esters in relation to the structure of the alkanol considered here. These factors also give rise to certain anomalies in the VLE behavior, such as will be observed later.

Vapor Pressures. Experimental vapor pressures for alkyl esters and the corresponding correlations have already been reported in other papers of this series. For that reason, Table 4 presents the data pairs (T,p_i°) only for the isobutylalkanol, which were obtained using the same experimental system as that for the VLE values. Table 5 lists the Antoine equation constants for the isobutylalkanol together with the values employed for all the pure components used in this study, citing the corresponding references. The mean differences between the Antoine curve for the isobutylalkanol obtained in this study and the curves published in the literature were in all cases smaller than 1% (see Table 5).

Reduction and Treatment of VLE Data. Table 6 gives the experimental T, x_1, and y_1 values obtained for isobaric equilibrium at (101.32 ± 0.02) kPa for the set of binary mixtures represented empirically as $CH_2(OH)CH(CH_3)_2$ (1) + $C_{u-1}H_{2u-1}COOC_vH_{2v+1}$ ($u = 1-4$; $v = 1-4$), with the exception of methyl methanoate, together with the quantities γ_1, γ_2, and G_m^E/RT, assuming the behavior of the vapor phase to be nonideal and calculating the activity coefficient values indirectly using the following expression:

$$\gamma_i = [\phi_i p y_i/(p_i^\circ x_i \phi_i^\circ)] \exp[(p_i^\circ - p)V_i^\circ/RT] \qquad (3)$$

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 the esters and the isobutylalkanol were either the literature values published by Spencer and Danner (1972) and Reid et al. (1988) or, when no literature values could be found, values calculated using the $V_i^\circ = f(T)$ data published by TRC, d-5030 (1966). The fugacity coefficients, ϕ_i and ϕ_i° in eq 3 were calculated using

$$\phi_i = \exp[(2\sum_k y_k B_{ik} - \sum_j \sum_k y_j y_k B_{jk})p/RT] \qquad (4)$$

where B_{ij} were the second virial coefficients for the pure components and their mixtures in the virial equation as calculated using the correlation of Tsonopoulos (1974). Reduction of the experimental values was performed using an equation similar to eq 1 to correlate the experimental data and applying the point-to-point test proposed by Fredenslund et al. (1977).

Figure 3 displays a matrix for the quantities ($y_1 - x_1$) and T on x_1 for the systems isobutylalkanol (1) + an alkyl alkanoates (2), including the methyl alkanoates published

Table 5. Coefficients A, B, and C of Antoine Equation[a] for the Pure Compounds Used in This Work

compound	A	B	C	s(p_i°)/kPa	T/K	ref
isobutylalkanol	6.875 90	1488.43	75.39	0.05	350−400	this work
	6.345 04	1190.38	106.48			Riddick et al. (1986)
	6.451 97	1248.48	100.30		293−388	Reid et al. (1988)
	6.586 46	1322.42	92.22		320−380	Linek (1979)
methyl ethanoate	6.493 40	1329.46	33.52		300−350	Ortega and Susial (1990b)
methyl propanoate	6.604 20	1478.55	30.07		310−370	Ortega and Susial (1990a)
methyl butanoate	6.303 60	1381.64	53.60		340−390	Ortega et al. (1990)
ethyl methanoate	6.647 55	1430.30	19.09		300−350	Soto et al. (1998)
ethyl ethanoate	6.572 59	1465.78	29.18		300−390	Hernández and Ortega (1997)
ethyl propanoate	6.334 31	1404.22	47.58		315−420	Hernández and Ortega (1997)
ethyl butanoate	6.360 31	1493.89	51.13		330−435	Hernández and Ortega (1997)
propyl methanoate	6.070 30	1181.20	63.30		320−375	González et al. (submitted)
propyl ethanoate	6.511 60	1524.56	36.19		320−430	González et al. (submitted)
propyl propanoate	6.011 27	1276.62	76.08		360−420	González et al. (submitted)
propyl butanoate	5.972 73	1331.40	80.07		375−440	González et al. (submitted)
butyl methanoate	6.708 20	1627.85	33.17		350−400	González and Ortega (1995)
butyl ethanoate	6.443 52	1584.05	42.20		350−450	González and Ortega (1995)
butyl propanoate	6.575 95	1745.90	36.04		350−450	González and Ortega (1995)
butyl butanoate	6.131 53	1500.71	74.43		400−480	González and Ortega (1995)

[a] $\log(p_i^\circ/\mathrm{kPa}) = A - B/[T/(\mathrm{K}) - C]$.

Table 6. Experimental Isobaric VLE Values at (101.32 ± 0.02) kPa for Binary Mixtures Isobutylalkanol (1) + Alkyl Esters (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
Isobutylalkanol (1) + Ethyl Methanoate (2)											
327.29	0.000	0.000		1.000	0.000	352.35	0.767	0.265	1.061	1.468	0.135
328.16	0.040	0.011	2.693	0.998	0.038	354.56	0.790	0.300	1.058	1.465	0.125
329.87	0.124	0.027	1.960	1.018	0.099	357.60	0.824	0.348	1.037	1.494	0.100
330.97	0.174	0.036	1.746	1.032	0.123	358.65	0.841	0.369	1.032	1.558	0.097
332.71	0.259	0.052	1.538	1.071	0.162	359.65	0.846	0.387	1.031	1.519	0.090
334.15	0.319	0.064	1.430	1.099	0.179	361.30	0.863	0.422	1.032	1.540	0.087
335.68	0.382	0.077	1.329	1.138	0.189	361.75	0.867	0.430	1.026	1.551	0.081
337.36	0.442	0.093	1.289	1.175	0.202	364.00	0.889	0.479	1.019	1.598	0.069
338.47	0.490	0.104	1.227	1.228	0.205	367.40	0.913	0.565	1.025	1.557	0.061
340.87	0.553	0.128	1.194	1.267	0.204	369.39	0.925	0.616	1.020	1.535	0.050
342.15	0.580	0.142	1.190	1.278	0.204	369.20	0.926	0.612	1.020	1.565	0.052
344.67	0.638	0.168	1.138	1.334	0.187	372.15	0.944	0.698	1.020	1.497	0.042
346.25	0.682	0.186	1.095	1.418	0.173	372.80	0.949	0.711	1.010	1.539	0.032
349.27	0.727	0.225	1.088	1.441	0.161	380.95	1.000	1.000	1.000		0.000
Isobutylalkanol (1) + Ethyl Ethanoate (2)											
350.25	0.000	0.000		1.000	0.000	361.39	0.533	0.286	1.128	1.090	0.105
350.47	0.013	0.007	1.846	0.996	0.004	363.23	0.603	0.334	1.080	1.136	0.097
350.96	0.042	0.021	1.658	0.996	0.017	364.15	0.634	0.361	1.068	1.153	0.094
351.06	0.045	0.024	1.692	0.994	0.018	365.25	0.671	0.393	1.054	1.180	0.090
351.57	0.079	0.040	1.596	0.998	0.035	366.80	0.708	0.440	1.052	1.175	0.083
352.49	0.111	0.059	1.616	0.985	0.040	368.05	0.746	0.480	1.038	1.210	0.076
354.33	0.211	0.110	1.469	0.992	0.075	369.75	0.784	0.537	1.035	1.211	0.068
354.43	0.220	0.113	1.443	0.997	0.078	371.01	0.816	0.580	1.024	1.245	0.060
355.37	0.278	0.136	1.322	1.019	0.091	372.56	0.846	0.638	1.023	1.235	0.052
356.48	0.333	0.162	1.253	1.035	0.098	374.39	0.884	0.707	1.016	1.255	0.040
357.43	0.372	0.186	1.234	1.039	0.102	375.95	0.913	0.769	1.009	1.274	0.030
358.33	0.415	0.209	1.196	1.056	0.106	377.65	0.943	0.842	1.007	1.263	0.020
359.39	0.457	0.235	1.171	1.065	0.106	380.95	1.000	1.000	1.000		0.000
360.37	0.494	0.260	1.149	1.076	0.106						
Isobutylalkanol (1) + Ethyl Propanoate (2)											
371.91	0.000	0.000		1.000	0.000	374.46	0.584	0.496	1.076	1.129	0.093
371.88	0.020	0.024	1.658	0.999	0.010	374.76	0.613	0.523	1.069	1.138	0.091
371.88	0.042	0.046	1.515	0.999	0.017	375.15	0.650	0.558	1.061	1.152	0.088
371.88	0.077	0.079	1.438	1.001	0.029	375.50	0.681	0.589	1.053	1.167	0.085
371.93	0.113	0.112	1.390	1.002	0.039	375.87	0.710	0.617	1.045	1.182	0.080
371.96	0.149	0.144	1.347	1.007	0.050	376.35	0.744	0.654	1.039	1.193	0.074
372.07	0.189	0.178	1.306	1.011	0.059	376.94	0.787	0.697	1.025	1.234	0.064
372.23	0.242	0.223	1.267	1.018	0.071	378.06	0.856	0.783	1.016	1.269	0.048
372.43	0.291	0.263	1.235	1.026	0.080	378.54	0.882	0.817	1.011	1.293	0.040
372.65	0.340	0.301	1.201	1.039	0.087	379.07	0.912	0.860	1.009	1.311	0.032
372.90	0.384	0.337	1.178	1.049	0.092	379.69	0.944	0.906	1.006	1.342	0.022
373.23	0.434	0.376	1.150	1.063	0.095	380.33	0.973	0.954	1.004	1.334	0.012
373.60	0.483	0.416	1.127	1.078	0.097	380.72	0.991	0.985	1.003	1.380	0.006
373.97	0.527	0.450	1.101	1.099	0.095	380.95	1.000	1.000	1.000		0.000
374.31	0.570	0.484	1.081	1.123	0.094						
Isobutylalkanol (1) + Ethyl Butanoate (2)											
394.17	0.000	0.000		1.000	0.000	383.15	0.553	0.635	1.066	1.122	0.087
392.18	0.061	0.111	1.247	1.001	0.015	382.83	0.586	0.662	1.060	1.133	0.086
390.83	0.108	0.187	1.243	1.002	0.025	382.50	0.621	0.692	1.058	1.139	0.084
389.82	0.145	0.236	1.207	1.010	0.036	382.20	0.666	0.723	1.041	1.174	0.080
388.75	0.187	0.293	1.206	1.013	0.046	381.90	0.710	0.756	1.033	1.198	0.076
387.65	0.239	0.355	1.186	1.020	0.056	381.66	0.752	0.788	1.024	1.229	0.069
386.75	0.289	0.406	1.156	1.031	0.064	381.46	0.793	0.821	1.019	1.252	0.061
385.96	0.331	0.449	1.146	1.041	0.072	381.27	0.840	0.858	1.012	1.296	0.051
385.25	0.374	0.490	1.133	1.051	0.078	381.16	0.873	0.885	1.008	1.326	0.043
384.65	0.416	0.530	1.123	1.059	0.081	381.07	0.907	0.915	1.006	1.349	0.033
384.15	0.450	0.560	1.118	1.066	0.085	381.00	0.940	0.944	1.004	1.379	0.023
383.84	0.482	0.583	1.096	1.084	0.086	380.97	0.974	0.976	1.003	1.383	0.011
383.45	0.516	0.610	1.085	1.099	0.088	380.95	1.000	1.000	1.000		0.000
Isobutylalkanol (1) + Propyl Methanoate (2)											
353.90	0.000	0.000		1.000	0.000	364.05	0.654	0.381	1.098	1.326	0.159
354.35	0.061	0.044	2.011	1.005	0.047	365.73	0.701	0.427	1.074	1.357	0.141
354.82	0.114	0.073	1.772	1.017	0.080	366.52	0.730	0.456	1.068	1.393	0.137
355.29	0.164	0.099	1.626	1.033	0.107	367.32	0.752	0.479	1.055	1.423	0.128
355.95	0.226	0.129	1.497	1.057	0.134	368.32	0.779	0.513	1.050	1.452	0.121
356.44	0.269	0.150	1.438	1.076	0.151	370.58	0.835	0.589	1.033	1.537	0.098
357.25	0.329	0.182	1.373	1.103	0.170	371.85	0.862	0.637	1.030	1.576	0.088
357.87	0.375	0.203	1.309	1.132	0.179	373.35	0.891	0.691	1.023	1.627	0.074
358.83	0.430	0.233	1.264	1.160	0.185	374.95	0.920	0.754	1.019	1.689	0.060
359.65	0.476	0.258	1.221	1.192	0.187	376.98	0.948	0.832	1.013	1.694	0.040
360.54	0.517	0.283	1.187	1.219	0.184	378.25	0.968	0.887	1.011	1.767	0.029
361.47	0.559	0.308	1.153	1.252	0.179	379.35	0.983	0.935	1.008	1.909	0.019
362.50	0.596	0.336	1.131	1.274	0.171	380.95	1.000	1.000	1.000		0.000
363.32	0.627	0.360	1.113	1.301	0.165						

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
Isobutylalkanol (1) + Propyl Ethanoate (2)											
374.31	0.000	0.000		1.000	0.000	375.75	0.589	0.522	1.071	1.123	0.088
374.19	0.034	0.037	1.410	1.007	0.018	375.95	0.615	0.546	1.065	1.132	0.087
374.15	0.073	0.077	1.357	1.007	0.029	376.15	0.639	0.567	1.056	1.145	0.084
374.10	0.125	0.128	1.312	1.010	0.043	376.43	0.665	0.593	1.051	1.151	0.080
374.10	0.175	0.173	1.269	1.016	0.055	376.67	0.692	0.617	1.042	1.168	0.077
374.15	0.224	0.217	1.243	1.020	0.064	376.96	0.721	0.645	1.033	1.189	0.072
374.25	0.268	0.256	1.219	1.025	0.072	377.25	0.751	0.676	1.029	1.204	0.068
374.36	0.314	0.294	1.189	1.036	0.078	377.59	0.780	0.709	1.026	1.214	0.063
374.49	0.356	0.328	1.166	1.045	0.083	377.94	0.808	0.737	1.017	1.245	0.056
374.64	0.395	0.360	1.150	1.054	0.087	378.45	0.850	0.787	1.013	1.276	0.048
374.80	0.433	0.391	1.129	1.067	0.089	378.85	0.881	0.826	1.012	1.294	0.041
374.96	0.469	0.421	1.115	1.079	0.091	379.34	0.913	0.868	1.008	1.326	0.032
375.17	0.502	0.448	1.101	1.089	0.091	379.91	0.949	0.920	1.008	1.349	0.023
375.36	0.533	0.474	1.091	1.099	0.091	380.95	1.000	1.000	1.000		0.000
375.55	0.562	0.498	1.079	1.113	0.090						
Isobutylalkanol (1) + Propyl Propanoate (2)											
395.55	0.000	0.000		1.000	0.000	383.75	0.543	0.640	1.072	1.109	0.085
393.89	0.045	0.091	1.314	0.998	0.010	383.63	0.551	0.649	1.076	1.103	0.084
392.09	0.099	0.182	1.259	1.002	0.025	383.24	0.589	0.678	1.065	1.120	0.084
390.70	0.150	0.254	1.224	1.006	0.036	382.96	0.618	0.698	1.057	1.137	0.083
389.73	0.186	0.304	1.216	1.008	0.043	382.70	0.647	0.720	1.049	1.153	0.081
388.88	0.223	0.346	1.190	1.017	0.052	382.39	0.685	0.747	1.040	1.176	0.078
388.13	0.256	0.383	1.175	1.025	0.059	382.09	0.726	0.777	1.031	1.203	0.073
387.45	0.287	0.417	1.165	1.031	0.066	381.81	0.767	0.807	1.023	1.236	0.067
386.81	0.319	0.450	1.157	1.037	0.071	381.62	0.800	0.832	1.018	1.262	0.061
386.28	0.350	0.479	1.143	1.045	0.076	381.43	0.834	0.858	1.013	1.296	0.054
385.71	0.385	0.513	1.135	1.050	0.079	381.27	0.868	0.884	1.009	1.333	0.046
385.28	0.416	0.539	1.118	1.061	0.081	381.11	0.899	0.910	1.008	1.363	0.039
384.86	0.447	0.566	1.107	1.069	0.083	380.99	0.934	0.938	1.006	1.428	0.029
384.59	0.469	0.584	1.101	1.075	0.083	380.91	0.961	0.962	1.005	1.484	0.020
384.36	0.488	0.599	1.093	1.082	0.084	380.95	1.000	1.000	1.000		0.000
384.02	0.516	0.621	1.085	1.093	0.085						
Isobutylalkanol (1) + Propyl Butanoate (2)											
416.41	0.000	0.000		1.000	0.000	390.33	0.491	0.739	1.097	1.091	0.090
412.70	0.043	0.130	1.119	1.004	0.009	389.21	0.533	0.765	1.084	1.112	0.093
411.73	0.054	0.161	1.129	1.006	0.012	388.10	0.577	0.790	1.075	1.133	0.095
410.60	0.070	0.199	1.119	1.008	0.015	387.25	0.612	0.810	1.068	1.148	0.094
407.32	0.116	0.302	1.121	1.013	0.025	386.55	0.650	0.828	1.054	1.177	0.091
405.85	0.136	0.344	1.139	1.015	0.031	385.73	0.690	0.848	1.044	1.210	0.089
404.35	0.160	0.386	1.131	1.021	0.038	385.21	0.723	0.864	1.033	1.233	0.082
402.84	0.186	0.429	1.133	1.024	0.043	384.48	0.761	0.882	1.028	1.266	0.078
401.21	0.213	0.474	1.147	1.023	0.047	383.88	0.797	0.899	1.021	1.304	0.070
399.35	0.249	0.524	1.151	1.025	0.054	383.27	0.834	0.917	1.016	1.343	0.062
395.05	0.343	0.627	1.143	1.045	0.075	382.71	0.871	0.934	1.011	1.385	0.052
394.10	0.371	0.650	1.130	1.053	0.078	382.15	0.906	0.951	1.008	1.450	0.042
392.67	0.411	0.683	1.121	1.066	0.085	381.63	0.943	0.969	1.005	1.554	0.030
392.38	0.422	0.690	1.113	1.073	0.086	380.95	1.000	1.000	1.000		0.000
391.29	0.457	0.716	1.106	1.081	0.088						
Isobutylalkanol (1) + Butyl Methanoate (2)											
379.89	0.000	0.000		1.000	0.000	376.55	0.515	0.489	1.114	1.147	0.122
378.86	0.058	0.083	1.550	0.987	0.013	376.57	0.542	0.510	1.103	1.164	0.122
378.37	0.099	0.132	1.458	0.992	0.031	376.62	0.570	0.532	1.092	1.182	0.122
377.78	0.152	0.188	1.396	1.002	0.053	376.69	0.598	0.553	1.078	1.207	0.120
376.90	0.246	0.282	1.327	1.025	0.088	376.79	0.627	0.577	1.070	1.226	0.118
376.73	0.278	0.304	1.276	1.042	0.098	376.93	0.658	0.602	1.059	1.251	0.114
376.65	0.302	0.323	1.250	1.052	0.103	377.09	0.690	0.630	1.050	1.278	0.110
376.56	0.326	0.340	1.226	1.064	0.108	377.32	0.721	0.658	1.041	1.304	0.103
376.51	0.349	0.359	1.207	1.073	0.112	377.55	0.754	0.688	1.032	1.339	0.096
376.48	0.370	0.375	1.192	1.082	0.114	377.86	0.791	0.723	1.023	1.384	0.086
376.48	0.391	0.393	1.176	1.090	0.116	378.21	0.826	0.760	1.016	1.432	0.075
376.48	0.411	0.406	1.163	1.099	0.117	378.62	0.861	0.800	1.010	1.479	0.063
376.48	0.412	0.409	1.169	1.095	0.118	379.12	0.896	0.843	1.005	1.529	0.049
376.48	0.437	0.427	1.148	1.111	0.119	380.33	0.967	0.946	1.002	1.601	0.017
376.50	0.439	0.430	1.152	1.106	0.119	380.75	0.989	0.981	1.001	1.690	0.007
376.50	0.464	0.450	1.139	1.119	0.121	380.95	1.000	1.000	1.000		0.000
376.52	0.489	0.468	1.124	1.134	0.121						

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
Isobutylalkanol (1) + Butyl Ethanoate (2)											
399.58	0.000	0.000		1.000	0.000	384.50	0.579	0.691	1.058	1.114	0.078
397.99	0.031	0.062	1.142	0.999	0.003	384.19	0.604	0.709	1.051	1.125	0.077
396.41	0.071	0.136	1.149	1.002	0.012	383.83	0.636	0.731	1.042	1.144	0.075
394.66	0.121	0.216	1.131	1.009	0.023	383.45	0.668	0.753	1.036	1.165	0.074
393.19	0.164	0.285	1.154	1.008	0.031	383.09	0.699	0.776	1.033	1.178	0.072
391.82	0.208	0.345	1.152	1.014	0.040	382.80	0.730	0.798	1.027	1.195	0.068
390.73	0.249	0.394	1.138	1.020	0.047	382.48	0.763	0.821	1.022	1.218	0.063
389.70	0.290	0.442	1.134	1.024	0.053	382.17	0.797	0.845	1.018	1.243	0.058
388.78	0.331	0.481	1.115	1.038	0.061	381.89	0.831	0.869	1.014	1.272	0.052
387.95	0.369	0.519	1.109	1.044	0.066	381.61	0.867	0.895	1.011	1.307	0.045
387.18	0.409	0.553	1.094	1.060	0.071	381.40	0.903	0.921	1.007	1.348	0.035
386.60	0.437	0.580	1.095	1.063	0.074	381.16	0.939	0.949	1.005	1.410	0.026
386.10	0.467	0.604	1.085	1.075	0.077	380.99	0.969	0.973	1.004	1.512	0.017
385.50	0.505	0.636	1.079	1.083	0.078	380.95	1.000	1.000	1.000		0.000
385.00	0.539	0.663	1.072	1.093	0.078						
Isobutylalkanol (1) + Butyl Propanoate (2)											
417.90	0.000	0.000		1.000	0.000	388.65	0.591	0.806	1.050	1.096	0.066
411.41	0.078	0.225	1.108	1.003	0.010	387.70	0.629	0.827	1.046	1.110	0.067
407.81	0.128	0.332	1.102	1.009	0.020	386.95	0.666	0.843	1.032	1.144	0.066
404.71	0.177	0.418	1.094	1.016	0.029	386.15	0.701	0.861	1.029	1.158	0.064
402.15	0.224	0.487	1.089	1.021	0.036	385.70	0.728	0.872	1.018	1.194	0.061
400.00	0.265	0.542	1.097	1.024	0.042	384.19	0.804	0.907	1.009	1.266	0.054
398.30	0.302	0.585	1.096	1.025	0.045	383.53	0.841	0.923	1.005	1.320	0.048
394.62	0.388	0.672	1.099	1.031	0.055	382.89	0.875	0.939	1.005	1.359	0.042
393.01	0.437	0.708	1.081	1.049	0.061	382.33	0.907	0.953	1.003	1.424	0.036
391.56	0.483	0.741	1.073	1.060	0.064	381.79	0.942	0.969	1.002	1.507	0.026
389.72	0.545	0.782	1.066	1.070	0.066	380.95	1.000	1.000	1.000		0.000
Isobutylalkanol (1) + Butyl Butanoate (2)											
438.32	0.000	0.000		1.000	0.000	389.35	0.634	0.899	1.067	1.128	0.085
423.50	0.088	0.371	1.154	1.008	0.020	388.15	0.678	0.912	1.053	1.161	0.083
412.18	0.193	0.588	1.139	1.024	0.044	387.30	0.714	0.921	1.039	1.207	0.081
409.35	0.228	0.637	1.134	1.023	0.046	386.50	0.749	0.931	1.029	1.241	0.075
403.75	0.304	0.721	1.133	1.033	0.061	385.50	0.787	0.942	1.024	1.276	0.071
396.40	0.437	0.814	1.115	1.070	0.086	384.65	0.825	0.952	1.017	1.317	0.062
394.95	0.473	0.833	1.103	1.080	0.087	383.79	0.863	0.963	1.013	1.339	0.051
393.40	0.507	0.852	1.107	1.074	0.087	382.95	0.899	0.972	1.011	1.394	0.043
392.42	0.536	0.863	1.096	1.088	0.088	382.13	0.935	0.982	1.010	1.450	0.033
391.75	0.554	0.871	1.092	1.092	0.088	381.40	0.967	0.991	1.011	1.511	0.024
391.50	0.563	0.874	1.089	1.093	0.087	381.00	0.987	0.996	1.010	1.624	0.016
390.60	0.593	0.885	1.077	1.111	0.087	380.95	1.000	1.000	1.000		0.000

earlier by Ortega and Susial (1995), the values being correlated directly using an equation similar to eq 1. The figure also presents the experimental ($y_1 - x_1$) values for certain mixtures already published in the literature for comparison. The quantities represented, T and ($y_1 - x_1$), followed a regular sequence with ester chain length both by row and by column as well as diagonally. The plots of ($y_1 - x_1$) for the mixture isobutylalkanol + butyl methanoate reveal sizable differences between the experimental values reported here and the values published by Seselkin et al. (1985), which were reported to be consistent according to the point-to-point test [see Gmehling et al. (1977), Vol. I/2f, p 308]. However, the differences were smaller with respect to the values for that same mixture published by Linek (1979). There was excellent agreement between the values for the mixtures consisting of isobutylalkanol (1) + butyl butanoate (2) and the values published by Volkova et al. (1979) [see Gmehling et al. (1977), Vol. I/2f, p 330], reported not to be consistent in the DECHEMA Collection with the point-to-point test by Fredenslund et al. (1977). Figure 4 plots the equimolar values for the quantity ($y_1 - x_1$) for each ester u and shows the variations to be quite linear. Because of the quasi-linear variation of this quantity with the chain length of the compounds, in our papers we prefer this representation instead of y versus x in order to present in the future an easier modelization. However, the matrix of y versus x also shows clear and regular variations according to the kind of mixtures, such as is known by the researchers.

Figure 5 also presents a matrix for the experimental values of the activity coefficients γ_i and the results for the adimensional form of the Gibbs function for the 15 mixtures comprising isobutylalkanol + an alkyl (methyl to butyl) alkanoate that have been studied at our laboratory. As pointed out in previous papers, the activity coefficients γ_i displayed maxima and minima in the regions of low isobutylalkanol concentration, giving rise to inflections in the Gibbs function. On the whole, anomalies of that type were mostly discernible in the mixtures containing the highest molecular weight esters, propanoate and butanoate, and this can be explained on the basis of the structural differences (size and shape) of the molecules involved, leading to increases in the S^E_m values. For mixtures containing isobutylalkanol the effects on H^E_m do not present a component so negative (exothermic) because of polar clumping as in other alkanols, with endothermicity prevailing as a result of the destruction of dipoles and hydrogen bonds in the alkanol. In short, the inflections in the G^E_m values were caused by the decrease in the H^E_m values in the regions of low alkanol concentration and the increase in the S^E_m values.

Figure 6 plots the equimolar values for the adimensional Gibbs function $Q^g = G^E_m/RT$ for each of the mixtures of isobutylalkanol with esters, empirically represented as $C_{u-1}H_{2u-1}COOC_vH_{2v+1}$, and shows a quasi-regular decrease as u increases that is qualitatively similar to the variations in other excess quantities already referred to above.

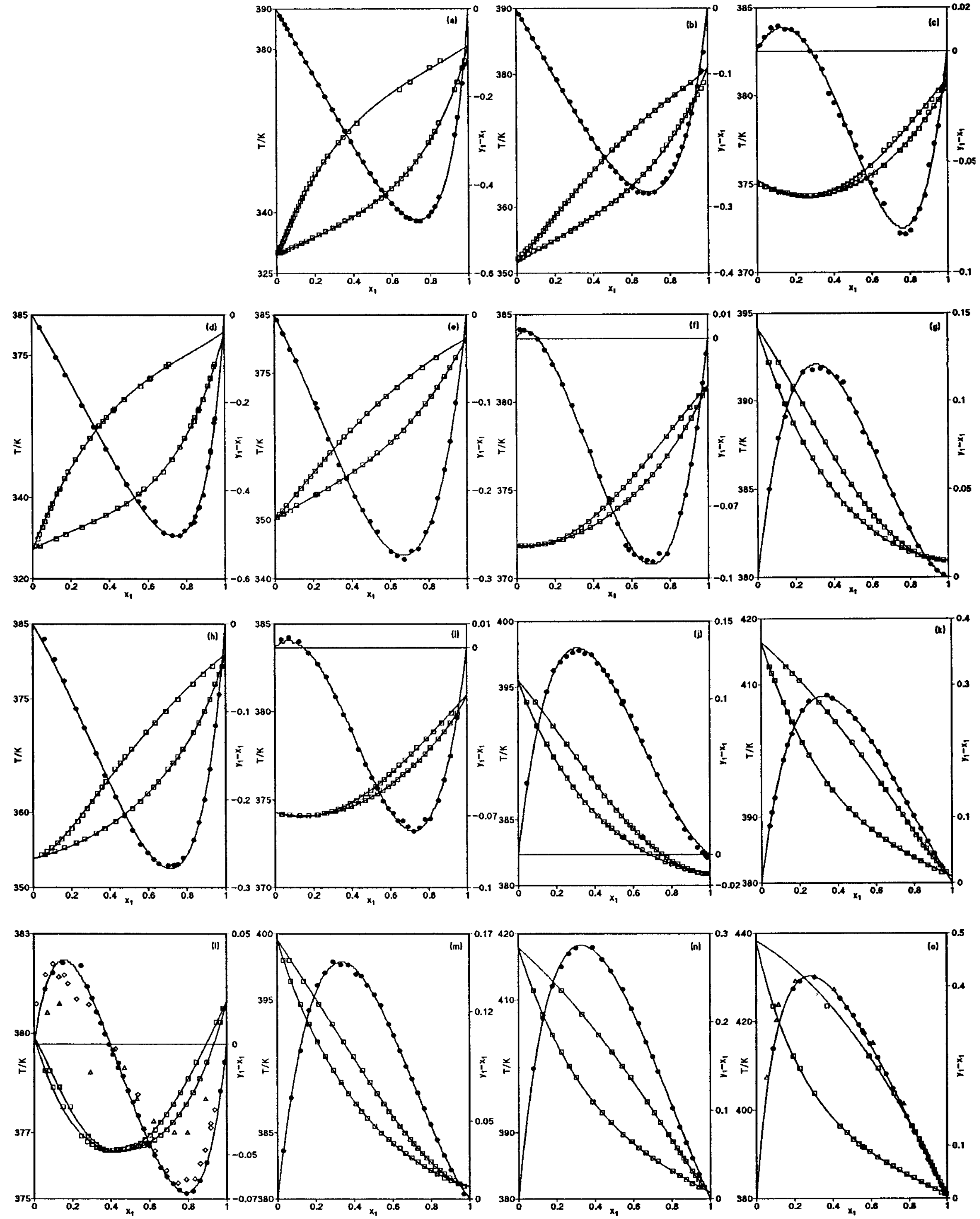

Figure 3. Representation of experimental values and curves for the quantities ($y_1 - x_1$) versus x_1 and T versus x_1, y_1 for 15 binary mixtures formed by isobutylalkanol (1) + alkyl esters (2): (a) methyl ethanoate; (b) methyl propanoate; (c) methyl butanoate; (d) ethyl methanoate; (e) ethyl ethanoate; (f) ethyl propanoate; (g) ethyl butanoate; (h) propyl methanoate; (i) propyl ethanoate; (j) propyl propanoate; (k) propyl butanoate; (l) butyl methanoate; (◇) from Linek (1979), (△) from Seselkin et al. (1985); (m) butyl ethanoate; (n) butyl propanoate; (o) butyl butanaote, (△) from Volkova et al. (1979) [see Gmehling et al. (1977), Vol. I/2f, p 330].

Mathematical-thermodynamic processing of the VLE data was carried out using a modified version of eq 1 in which the coefficients in the polynomial equation were made temperature-dependent. The values of the adimen-

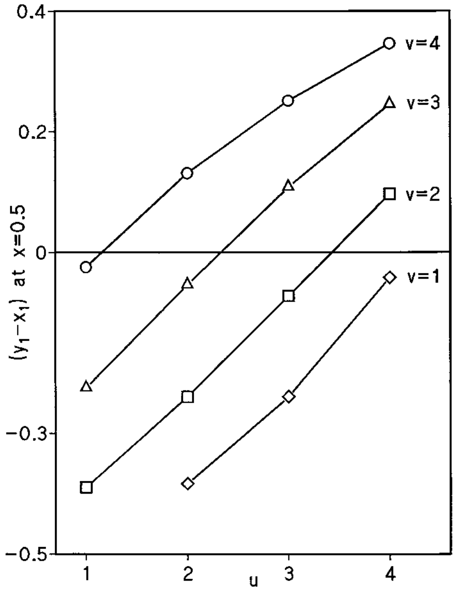

Figure 4. Variation of the quantities $(y_1 - x_1)$ obtained experimentally in the isobaric VLE for the binary mixtures isobutylalkanol (1) + $C_{u-1}H_{2u-1}COOC_vH_{2v+1}$ (2) as a function of number of carbon atoms in the alkyl alkanoate, *u*, and *v*.

sional function $Q^g = G^E_m/RT$ for the mole fraction x_1 of the component common to all the mixtures, isobutylalkanol, were used to that end. The equation was put forward in an earlier paper by Soto et al. (1998) and takes the form

$$Q^g = x_1x_2\left[\left(\frac{A_{01}}{T} + A_{02}\right) + \left(\frac{A_{11}}{T} + A_{12}\right)z + \left(\frac{A_{21}}{T} + A_{22}\right)z^2 + \ldots\right] \quad (5)$$

where *z* was expressed as a function of the mole fraction as in eq 1 and *k* was calculated in the fitting procedure. The advantage of this kind of equation is that using an expression identical to eq 1 in the same way allows that its coefficients be related to the corresponding coefficients in the enthalpies correlation. The correspondence is readily observable in the correlation of the excess enthalpy data written in adimensional form:

$$\frac{H^E_m}{RTx_1x_2}\sum A^1_i z^i \quad (6)$$

in that a simple relationship for the coefficients in eqs 5 and 6, $A^1_i = A_{i1}/T$, is readily obtainable taking into account the thermodynamic expression $H^E_m = [\partial(G^E_m/T)/\partial(1/T)]_{px}$. Thus, once the first coefficients in eq 5 have been obtained (A^1_i values directly from the correlation of the enthalpies), then the A_{i2} values in eq 5 can be calculated using the isobaric VLE values G^E_m/RT and γ_i simultaneously.

For that case, the objective function used was defined as

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

where $Y = \gamma_j$, $Q^g = G^E_m/RT$, and $Q^h = H^E_m/RT$ and fits were calculated using the Solver computational subroutine from the Excel (Microsoft) spreadsheet program, version 5.0a. The results obtained appear in Table 7 together with the standard deviation values for each of the correlated quantities. Correlations were excellent for all the quantities included in the fitting procedure, and the corresponding curves are shown in Figure 5 for all mixtures. The largest differences of the global objective function (eq 8) were recorded for the set of properties of the mixture consisting of isobutylalkanol + methyl methanoate, mainly due to the high discrepancies existing in the correlation of the γ_i values (see Figure 5a); however, the correlations of excess enthalpies were good in all cases because the differences never exceeded 4%.

Table 7. Fitting Coefficients Obtained in Correlation of VLE Data and Excess Enthalpies of Binary Mixtures Isobutylalkanol (1) + Alkyl Esters (2) Using Eq 5 and Standard Deviation for Quantities $Y = \gamma_i$, $Q^g = G^E_m/RT$, and $Q^h = H^E_m/RT$

	coefficient		$s(Y)$	$s(Q^g)$	$s(Q^h)$
	Isobutylalkanol (1) + Methyl Ethanoate (2)				
$k = 0.47^a$	$A_{01} = 1071.8$	$A_{02} = -2.570$	0.082	0.009	0.01
	$A_{11} = -76.2$	$A_{12} = 0.340$			
	Isobutylalkanol (1) + Methyl Propanoate (2)				
$k = 0.55^a$	$A_{01} = 1129.1$	$A_{02} = -2.843$	0.050	0.006	0.03
	$A_{11} = -216.6$	$A_{12} = 0.890$			
	Isobutylalkanol (1) Methyl Butanoate (2)				
$k = 0.60^a$	$A_{01} = 1091.2$	$A_{02} = -2.527$	0.017	0.003	0.03
	$A_{11} = -233.9$	$A_{12} = 0.705$			
	Isobutylalkanol (1) + Ethyl Methanote (2)				
$k = 0.11^a$	$A_{01} = 1486.9$	$A_{02} = -3.393$	0.054	0.011	0.01
	$A_{11} = -559.8$	$A_{12} = 1.464$			
	Isobutylalkanol (1) + Ethyl Ethanoate (2)				
$k = 1.04^a$	$A_{01} = 973.2$	$A_{02} = -2.219$	0.030	0.007	0.01
	$A_{11} = -145.6$	$A_{12} = 0.332$			
	Isobutylalkanol (1) + Ethyl Propanoate (2)				
$k = 0.50^a$	$A_{01} = 964.0$	$A_{02} = -2.151$	0.024	0.004	0.01
	$A_{11} = -176.1$	$A_{12} = 0.423$			
	Isobutylalkanol (1) + Ethyl Butanoate (2)				
$k = 0.15^a$	$A_{01} = 1071.8$	$A_{02} = -2.517$	0.009	0.002	0.01
	$A_{11} = -284.8$	$A_{12} = 0.819$			
	Isobutylalkanol (1) + Propyl Methanoate (2)				
$k = 0.15^a$	$A_{01} = 900.0$	$A_{02} = -1.711$	0.036	0.007	0.01
	$A_{11} = -27.3$	$A_{12} = 0.000$			
	Isobutylalkanol (1) + Propyl Ethanoate (2)				
$k = 5.20^a$	$A_{01} = 842.4$	$A_{02} = -1.891$	0.006	0.002	0.01
	$A_{11} = -55.8$	$A_{12} = 0.202$			
	Isobutylalkanol (1) + Propyl Propanoate (2)				
$k = 1.78^a$	$A_{01} = 853.1$	$A_{02} = -1.904$	0.009	0.002	0.01
	$A_{11} = -111.8$	$A_{12} = 0.370$			
	Isobutylalkanol (1) + Propyl Butanoate (2)				
$k = 1.12^a$	$A_{01} = 847.8$	$A_{02} = -1.891$	0.014	0.003	0.01
	$A_{11} = -93.9$	$A_{12} = 0.407$			
	Isobutylalkanol (1) + Butyl Methanoate (2)				
$k = 0.18^a$	$A_{01} = 1132.6$	$A_{02} = -2.534$	0.023	0.005	0.01
	$A_{11} = -303.0$	$A_{12} = 0.841$			
	Isobutylalkanol (1) + Butyl Ethanoate (2)				
$k = 1.75^a$	$A_{01} = 869.6$	$A_{02} = -2.006$	0.013	0.002	0.01
	$A_{11} = -66.3$	$A_{12} = 0.320$			
	Isobutylalkanol (1) + Butyl Propanoate (2)				
$k = 2.60^a$	$A_{01} = 994.3$	$A_{02} = -2.339$	0.025	0.009	0.09
	$A_{11} = -235.2$	$A_{12} = 0.886$			
	Isobutylalkanol (1) + Butyl Butanoate (2)				
$k = 0.11^a$	$A_{01} = 1041.5$	$A_{02} = -2.307$	0.033	0.04	0.01
	$A_{11} = -267.5$	$A_{12} = 0.696$			

[a] Obtained by fit. $s(X) = [\sum_{i=1}^N (X_{i,\mathrm{exp}} - X_{i,\mathrm{cal}})^2/(N - n)]^{1/2}$, N = number of experimental points, and n = number of coefficients.

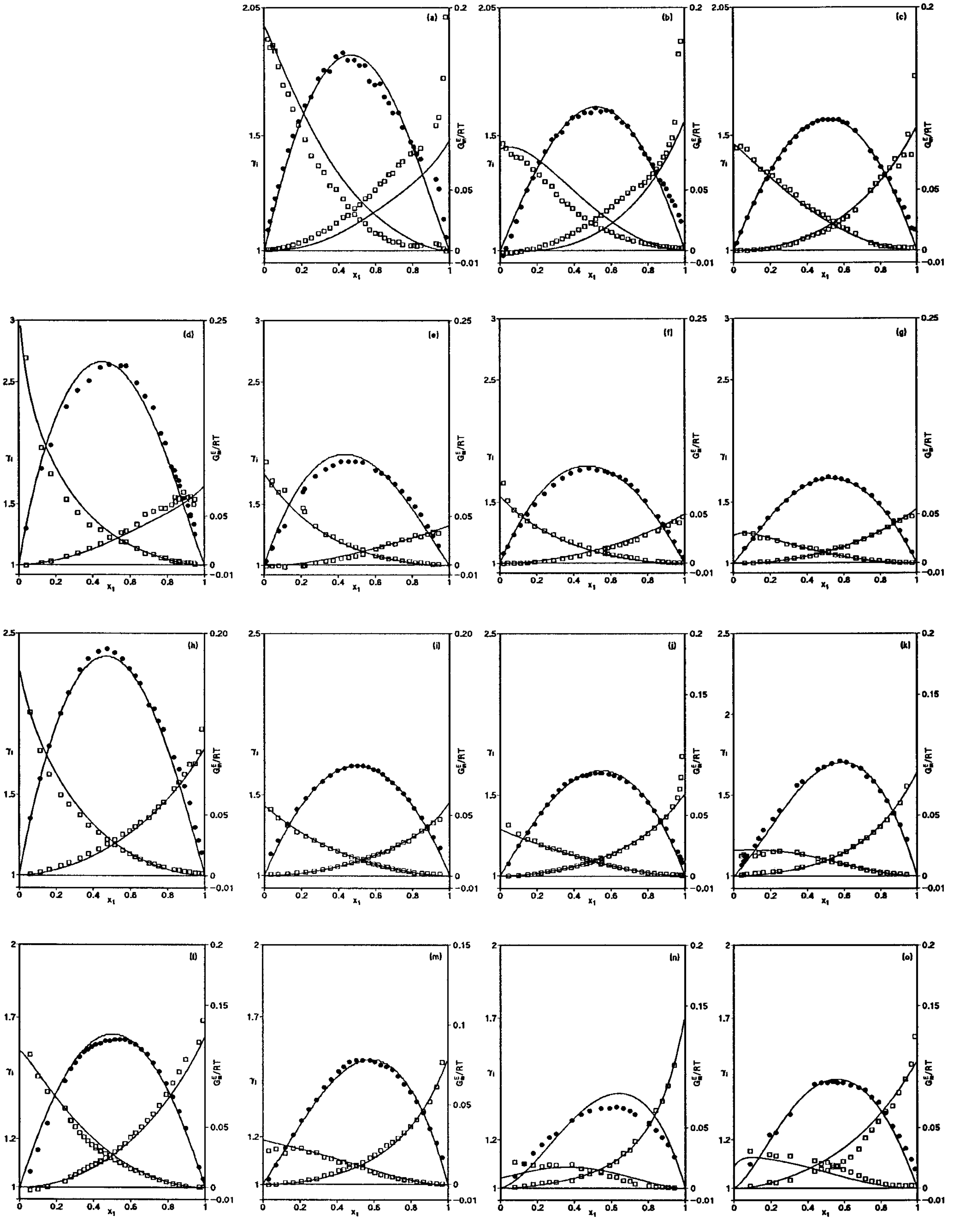

Figure 5. Representation of experimental values and curves for the quantities G^E_m/RT versus x_1 and γ_i versus x_1 for 15 binary mixtures formed by isobutylalkanol (1) + alkyl esters (2): (a) methyl ethanoate; (b) methyl propanoate; (c) methyl butanoate; (d) ethyl methanoate; (e) ethyl ethanoate; (f) ethyl propanoate; (g) ethyl butanoate; (h) propyl methanoate; (i) propyl ethanoate; (j) propyl propanoate; (k) propyl butanoate; (l) butyl methanoate; (m) butyl ethanoate; (n) butyl propanoate; (o) butyl butanoate.

Azeotropes. Only five mixtures from the set of 15 isobutylalkanol (1) + an alkyl ester (2) mixtures considered in this paper had azeotropes. The values of the singular points for the binary mixtures given in Table 8 were

Table 8. Experimental Azeotropes Found in Binary Systems Isobutylalkanol (1) + Alkyl Esters (2) and Comparison with Literature and Predicted Values

mixture	azeotropic points		ref
	x^a	T/K	
isobutylalkanol (1) +			
methyl butanoate (2)	0.285	374.3	Ortega and Susial (1995)
	0.315	374.4	Gmehling et al. (1994)
	0.313	373.5	predicted by ASOG, Tochigi et al. (1990)
	0.263	374.0	predicted by UNIFAC, Gmehling et al. (1993)
	0.323	372.3	predicted by UNIFAC, Hansen et al. (1991)
ethyl propanoate (2)	0.112	371.93	this work
	0.171	<372.05	Gmehling et al. (1994)
	0.207	371.3	predicted by ASOG, Tochigi et al. (1990)
	0.217	371.6	predicted by UNIFAC, Gmehling et al. (1993)
	0.262	370.3	predicted by UNIFAC, Hansen et al. (1991)
propyl ethanoate (2)	0.169	374.10	this work
	0.244	374.15	Gmehling et al. (1994)
	0.302	373.1	predicted by ASOG, Tochigi et al. (1990)
	0.127	374.4	predicted by UNIFAC, Gmehling et al. (1993)
	0.317	372.1	predicted by UNIFAC, Hansen et al. (1991)
propyl propanoate (2)	0.967	380.90	this work
	0.897	380.6	predicted by ASOG, Tochigi et al. (1990)
	0.982	380.9	predicted by UNIFAC, Gmehling et al. (1993)
	0.777	380.0	predicted by UNIFAC, Hansen et al. (1991)
butyl methanoate (2)	0.402	376.48	this work
	0.418	377.4	Linek (1979)
	0.239	376.10	Seselkin et al. (1985)
	0.479	376.15	Gmehling et al. (1994)
	0.457	376.0	predicted by ASOG, Tochigi et al. (1990)
	0.447	375.5	predicted by UNIFAC, Gmehling et al. (1993)
	0.447	374.2	predicted by UNIFAC, Hansen et al. (1991)

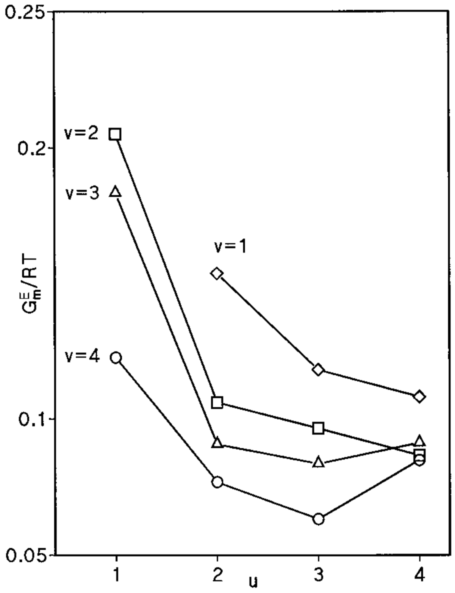

Figure 6. Variation of the adimensional Gibbs function G_m^E/RT as a function of number of carbon atoms in the alkyl alkanoate, *u*, and *v*, obtained from isobaric VLE data of the binary mixtures isobutylalkanol (1) + $C_{u-1}H_{2u-1}COOC_vH_{2v+1}$ (2).

calculated using the contour conditions $(y_1 - x_1) = 0$, $(\partial T/\partial x_1)_p = 0$, and $(\partial T/\partial y_1)_p = 0$ and the plots shown in Figure 2, and the results are compared with the literature values. As mentioned in the Introduction, some of the literature values for the azeotropes differed appreciably among themselves and from the values calculated in this study, particularly with respect to the concentrations. On comparison, the closest concentration value was for the mixture comprising isobutylalkanol + butyl methanoate and the values published by Linek (1979), though the difference in the temperature was around 1 K. The VLE values cast doubt about the azeotrope, in that the minimum boiling temperature does not correspond to the value of $(y_1 - x_1) = 0$. The literature did not disclose any estimate for the azeotrope for the mixture composed of isobutylalkanol + propyl propanoate, which was detected experimentally at high alkanol concentrations. The scarcity of data for other temperature and pressure conditions precluded calculation of the corresponding azeotropic lines, as has been done in other papers of this kind, and hence future work could present VLE experiments carried out under other conditions.

Prediction of VLE. As in other papers, some of the best known group contribution models were again used to predict the isobaric vapor−liquid equilibrium quantities, namely, the ASOG model of Tochigi et al. (1990), the original UNIFAC model using the parameters put forward by Hansen et al. (1991), and the modified version of the UNIFAC model using the parameter values published by Gmehling et al. (1993).

The modified-UNIFAC model as revised by Gmehling et al. (1993) was the model that yielded the best match to the experimental data points, differentiating the methanoate-containing mixtures from the nonmethanoate-containing mixtures, with mean differences in the activity coefficient values that in no case exceeded 5%. The original version of the UNIFAC model yielded acceptable results for the mixtures containing methanoates, but for mixtures containing the other esters, the discrepancies increased with ester chain length, reaching up to 25% for butyl butanoate. Using the same interaction pair, OH/COO, for all components, the ASOG model also provided good estimates for the mixtures containing methanoates, but here too the differences increased for the highest molecular weight esters; still, the usefulness of the method proved to be acceptable, in that the differences did not exceed 9%.

The prediction of the different azeotropic points obtained using the modified-UNIFAC model was only fair, in that it predicted the presence of a singular point for the mixture comprising isobutylalkanol + ethyl propanoate that was not found experimentally, though on the other hand it rightly predicted an azeotrope for the mixture composed of isobutylalkanol + propyl propanoate that was not found in the literature but was revealed by the experimental results. The results of the other models for that same mixture were very different from the experimental results.

The excess enthalpies presented in Table 2 were also calculated using the modified-UNIFAC model with the set of parameter values published by Gmehling et al. (1993). The values were in all cases lower than the experimental values, with differences for the set of mixtures ranging from 12 to 26%.

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