Densities and Isobaric Vapor−Liquid Equilibria for the Mixtures Formed by Four Butyl Esters and 1-Butanol

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Densities of 298.15 K and the vapor−liquid equilibria for 1-butanol + butyl methanoate, + butyl ethanoate, + butyl propanoate, and + butyl butanoate have been measured at 101.32 kPa in a small capacity ebulliometer. All results were found to be thermodynamically consistent with a point-to-point test. The mixtures containing butyl methanoate and butyl ethanoate show azeotropes at $T = 379.14$ K, $x = 0.871$ and $T = 389.64$ K, $x = 0.222$, respectively. Different group-contribution methods were applied to these mixtures.

Introduction

Continuing a series of studies carried out in our laboratory on the isobaric vapor−liquid equilibria (VLEs) of mixtures of butyl esters and ethanol (González and Ortega, 1995a) and 1-propanol (González and Ortega, 1995b), this paper presents VLE measurements on the first four butyl esters (from methanoate to butanoate) with 1-butanol. The literature contains values for the mixture butyl ethanoate + 1-butanol [Beregovykh et al., 1971 (see Gmehling et al., 1982, p 197); Brunjes and Furnas, 1935; Sheinker and Peresleni, 1952 (see Gmehling et al., 1978, pp 194, 197); Figurski and von Weber, 1977; Mato and Cepeda, 1985; Ortega et al., 1987)] and for the mixture butyl butanoate + 1-butanol (Volkova et al., 1979 (see Gmehling et al., 1990, p 205)]. Despite these earlier measurements it was decided to make additional experimental measurements with a modified ebulliometer and with a view to completing an updated, systematic study of this family of binary mixtures that would enhance our understanding of their behavior.

The literature on such systems estimates minimum azeotropes for butyl methanoate (1) + 1-butanol (2) and butyl ethanoate (1) + 1-butanol (2), at $x_1 = y_1 = 0.701$, $T = 378.95$ K for the former and $x_1 = y_1 = 0.237$, $T = 390.75$ K for the latter (Horsley, 1952).

Experimental Section

Components. 1-Butanol (puriss. p.a. >99.5 mol % from Fluka) and the esters were degassed using ultrasound prior to use and dried on molecular sieves (0.3 nm from Fluka). The most important physical properties of the alcohol were determined experimentally, and the following quantities were obtained: ρ(298.15 K) = 805.68 kg·m^{-3}, 805.75 kg·m^{-3} (Riddick et al., 1986) 806.0 kg·m^{-3} (TRC, 1993); n(D, 298.15 K) = 1.3971, 1.39741 (Riddick et al., 1986), 1.3973 (TRC, 1993); T_b = 390.77 K, 390.87 K (Riddick et al., 1986), 390.81 K (TRC, 1993).

Equipment and Procedure. The ebulliometer was the same used by us in previous works on VLE. An Anton Paar Model DMA-55 vibrating-tube densimeter calibrated with water and nonane was used to analyze the samples of the liquid and vapor phases; the phase compositions were calculated using a correlation for densities of the type $\rho = \sum A_i x_1^i$, and the precision for the mole fraction was ±0.001. These were not significantly different from the values calculated using the correlation for the excess molar volume, V_m^E.

Experimental Results

Densities and Excess Volumes. Table 1 presents the experimental values for concentration, x_1, and ρ at (298.15 ± 0.01) K for each of the binary butyl ester (1) + 1-butanol (2) systems considered. The precisions of the calculations were ±10^{-4} for the mole fraction, ±0.02 kg·m^{-3} for the densities, and ±2 × 10^{-9} m^3·mol^{-1} for the V_m^E values. The excess molar volumes were correlated using the following polynomial equation:

$$10^9 V_m^E/(\mathrm{m^3{\cdot}mol^{-1}}) = x_1(1 - x_1)\sum A_i[x_1/(x_1 + kx_2)]^i \qquad (1)$$

Table 2 gives the values of the coefficients A_i and k for each of the mixtures, calculated by a method of linear regression including minimization of the corresponding standard deviation, $s(V_m^E)$, values. The literature contained V_m^E values for the mixtures butyl methanoate + 1-butanol (Ortega, 1985) and butyl ethanoate + 1-butanol (Ortega et al., 1985). No relevant discrepancies were observed for the butyl methanoate + 1-butanol system, with a difference of 2 × 10^{-9} m^3·mol^{-1} at $x_1 = 0.5$. For the mixture of butyl ethanoate + 1-butanol, the difference in the V_m^E values was estimated at 16%, namely, 18 × 10^{-9} m^3·mol^{-1} at $x_1 = 0.5$. Figure 1 graphically plots the experimental V_m^E values and the fitting curves for the systems considered using eq 1, along with the curves presented in the literature. In view of the marked discrepancies between the V_m^E values reported here and the values published previously by our laboratory for the mixture butyl ethanoate + 1-butanol, the equimolar values, $V_m^E(x_1 = 0.5)$, for the various alcohols were plotted versus butyl ester chain length (Figure 2) (González and Ortega, 1995a,b). The value for the mixture of butyl ethanoate + 1-butanol was then somewhat higher than the value published earlier (Ortega et al., 1985) but was more in agreement with the behavior of the other mixtures. The plots of the equimolar V_m^E values yielded intersecting curves; this is not surprising and is a consequence of the properties of these systems, an aspect currently under study in our laboratory.

Vapor-Liquid Equilibrium Data. Table 3 gives the experimental $T-x_1-y_1$ vapor−liquid equilibrium values at (101.32 ± 0.02) kPa for the butyl ester (1) + 1-butanol (2) mixtures and the activity coefficients for the liquid phase, γ_i, calculated using the equation

$$\phi_i p y_i = \gamma_i p_i^o x_1 \phi_i^o \exp[v_i^L(p - p_i^o)/RT] \qquad (2)$$

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Table 1. Densities and Excess Volumes for Butyl Alkanoates (1) + 1-Butanol (2) a 298.15 K

x_1	ρ/(kg·m^{-3})	$10^9V_m^E$/(m^3·mol^{-1})	x_1	ρ/(kg·m^{-3})	$10^9V_m^E$/(m^3·mol^{-1})
		Butyl Methanoate (1) + 1-Butanol (2)			
0.0774	812.93	55	0.4638	846.46	178
0.1282	817.62	80	0.5257	851.44	180
0.1620	820.61	106	0.6002	857.33	172
0.2009	824.08	123	0.6856	863.91	155
0.2576	829.10	140	0.7291	867.21	143
0.2696	830.14	145	0.7893	871.73	119
0.2994	832.70	154	0.8859	878.79	74
0.3432	836.41	168	0.9416	882.82	37
0.3970	840.93	176			
		Butyl Ethanoate (1) + 1-Butanol (2)			
0.0475	810.05	44	0.5062	846.11	196
0.0879	813.67	71	0.5687	850.32	188
0.1330	817.61	98	0.6445	855.20	178
0.1815	821.74	119	0.7041	858.94	158
0.2466	827.05	145	0.7641	862.49	148
0.3162	832.47	166	0.8441	867.15	115
0.3784	837.14	178	0.9309	872.07	60
0.4552	842.61	191			
		Butyl Propanoate (1) + 1-Butanol (2)			
0.0424	809.78	34	0.5134	845.97	149
0.1049	815.67	55	0.5924	850.65	149
0.1582	820.32	78	0.6851	855.76	145
0.2018	823.94	93	0.7473	858.98	139
0.2504	827.79	108	0.7777	860.52	132
0.2857	830.48	117	0.8136	862.29	124
0.3374	834.25	130	0.8909	866.01	92
0.4063	839.03	137	0.9233	867.54	72
0.4627	842.71	143	0.9686	869.68	33
		Butyl Butanoate (1) + 1-Butanol (2)			
0.0486	810.50	19	0.4714	841.18	137
0.0947	814.73	40	0.5842	847.11	142
0.1723	821.26	71	0.7528	854.85	126
0.2247	825.32	85	0.8222	857.72	110
0.2892	829.91	107	0.9185	861.52	65
0.3441	833.56	119	0.9349	862.15	54

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

mixture	k	A_0	A_1	A_2	$10^9s(V^E)$/(m^3·mol^{-1})
butyl methanoate (1) + 1-butanol (2)	0.04	335	1140	−765	2
butyl ethanoate (1) + 1-butanol (2)	1.06	911	−651	699	3
butyl propanoate (1) + 1-butanol (2)	1.76	636	−538	1105	2
butyl butanoate (1) + 1-butanol (2)	4.09	469	430	161	2

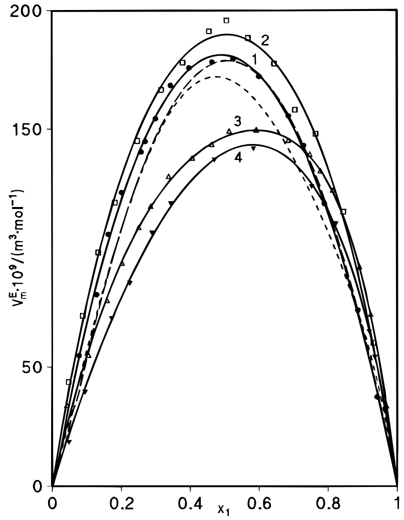

Figure 1. Excess volumes, V_m^E, at 298.15 K for the binaries $C_{u-1}H_{2u-1}CO_2C_4H_9$ (1) + $CH_3(CH_2)_3OH$ (2). Numbers indicate u. Key: (●) methanoate; (box) ethanoate; (△) propanoate; (▼) butanoate; (— — —) Ortega (1985); (- - -) Ortega et al. (1985).

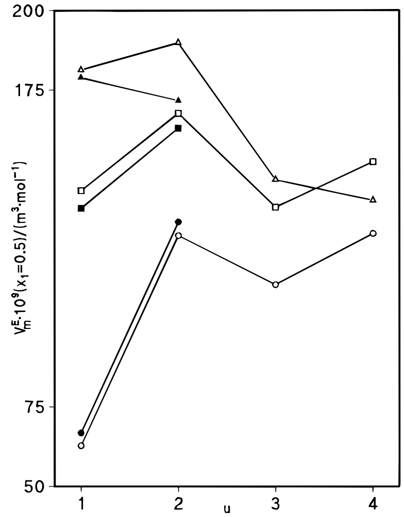

Figure 2. Representation of equimolar excess volumes at 298.15 K, $V_m^E(x_1=0.5)$, for the mixtures $C_{u-1}H_{2u-1}CO_2C_4H_9$ (1) + 1-alcohols (2), as a function of u: (○) ethanol; (□) 1-propanol; (△) 1-butanol. Comparison with the literature values for butyl methanoates (Ortega, 1985) and butyl ethanoates (Ortega et al., 1985).

A modified version of Rackett's equation (Spencer and Danner, 1972) was used to obtain the variation in the molar volumes with the equilibrium temperature, and the virial equation (truncated at the second term) was used to calculate the values of the fugacity coefficients, ϕ_i, and ϕ_i^o, such that

$$\phi_i = \exp[(p/RT)(2\sum y_iB_{ij} - \sum\sum y_iy_jB_{ij})] \tag{3}$$

The second virial coefficients for both the pure components and the mixtures of the components were calculated employing the equations proposed by Tsonopoulos (1974). The vapor pressure values, p_i^o, were calculated using the Antoine equation, whose constants A, B, and C had already been computed in our laboratory and reported earlier for 1-butanol (Susial and Ortega, 1993) and the butyl esters (González and Ortega, 1995a).

The four mixtures considered here were consistent using the point-to-point test as published by Fredenslund et al. (1977b). The experimental composition data were fitted using the following polynomial equation, similar to eq 1:

$$Q = x_1x_2\sum A_i[x_1/(x_1 + kx_2)]^i \tag{4}$$

where $Q = (y_1 - x_1)$. Correlation of temperature, T, with ester composition in the liquid phase, x_1, and the vapor phase, y_1, was performed using the following equation:

$$T = x_1T_{b,1}^o + x_2T_{b,2}^o + Q \tag{5}$$

where Q represents eq 4 and $T_{b,1}^o$ and $T_{b,2}^o$ are the boiling temperatures of pure components 1 and 2, respectively. Substituting y_1 for x_1 in eq 5 yields the correlation of T with y_1. The values of the coefficients A_i and k and the corresponding standard deviations, s, obtained by fitting the corresponding functions, appear in Table 4. Figures 3 and 4 plot the experimental VLE data and the fitting curves for the four mixtures considered here. Only the mixtures butyl methanoate (1) + 1-butanol (2) and butyl

Table 3. Vapor–Liquid Equilibrium Data for Butyl Alkanoates (1) + 1-Butanol (2) at 101.32 kPa

T/K	X_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
				Butyl Methanoate (1) + 1-Butanol (2)					
389.83	0.0105	0.0235	1.656	1.000	381.17	0.4469	0.5686	1.206	1.073
389.44	0.0269	0.0579	1.616	0.994	380.88	0.4710	0.5882	1.194	1.083
388.67	0.0522	0.1112	1.631	0.989	380.63	0.4970	0.6086	1.179	1.092
387.72	0.0903	0.1790	1.560	0.984	380.39	0.5241	0.6233	1.153	1.121
386.90	0.1180	0.2247	1.532	0.986	380.29	0.5508	0.6451	1.139	1.123
386.23	0.1508	0.2722	1.479	0.984	380.20	0.5604	0.6529	1.136	1.126
385.33	0.1967	0.3263	1.395	0.994	379.95	0.5962	0.6794	1.119	1.142
384.58	0.2295	0.3687	1.380	0.997	379.63	0.6361	0.7092	1.106	1.163
383.86	0.2632	0.4060	1.353	1.007	379.44	0.6934	0.7418	1.067	1.235
383.25	0.2977	0.4416	1.324	1.015	379.26	0.7389	0.7778	1.055	1.257
382.70	0.3312	0.4712	1.290	1.029	379.16	0.8099	0.8207	1.019	1.399
382.23	0.3630	0.4997	1.265	1.040	379.14	0.8712	0.8711	1.005	1.484
381.87	0.3937	0.5260	1.241	1.049	379.26	0.9375	0.9297	0.994	1.663
381.49	0.4207	0.5480	1.223	1.061	379.28	0.9774	0.9714	0.995	1.875
				Butyl Ethanoate (1) + 1-Butanol (2)					
390.13	0.0271	0.0322	1.531	0.998	390.71	0.4806	0.4156	1.095	1.107
389.96	0.0629	0.0761	1.570	0.995	390.82	0.4961	0.4318	1.099	1.106
389.90	0.0892	0.1067	1.554	0.992	390.97	0.5159	0.4449	1.084	1.119
389.82	0.1342	0.1434	1.391	1.003	391.29	0.5521	0.4769	1.076	1.128
389.72	0.1625	0.1718	1.380	1.006	391.67	0.5964	0.5126	1.059	1.151
389.65	0.1981	0.2010	1.327	1.017	392.13	0.6401	0.5513	1.047	1.170
389.69	0.2411	0.2256	1.222	1.039	392.60	0.6797	0.5885	1.039	1.187
389.76	0.2789	0.2515	1.175	1.055	393.25	0.7269	0.6377	1.033	1.200
389.84	0.3034	0.2781	1.191	1.050	393.77	0.7659	0.6753	1.023	1.233
389.94	0.3346	0.3036	1.175	1.057	394.42	0.8023	0.7182	1.020	1.240
390.07	0.3759	0.3285	1.128	1.082	395.12	0.8449	0.7665	1.013	1.280
390.15	0.3913	0.3464	1.140	1.077	395.89	0.8842	0.8157	1.009	1.321
390.32	0.4245	0.3701	1.117	1.092	396.59	0.9168	0.8679	1.015	1.287
390.48	0.4505	0.3917	1.109	1.098	397.43	0.9570	0.9196	1.007	1.475
390.65	0.4783	0.4134	1.097	1.109					
				Butyl Propanoate (1) + 1-Butanol (2)					
390.78	0.0357	0.0232	1.412	0.994	395.54	0.3992	0.2396	1.127	1.060
390.85	0.0620	0.0430	1.506	0.999	395.79	0.4169	0.2476	1.107	1.072
391.30	0.1027	0.0690	1.436	1.000	396.38	0.4521	0.2691	1.090	1.087
391.72	0.1446	0.0945	1.380	1.006	396.43	0.4524	0.2694	1.089	1.085
392.31	0.1880	0.1196	1.318	1.010	397.18	0.4893	0.2923	1.068	1.100
392.85	0.2309	0.1444	1.274	1.018	398.18	0.5303	0.3215	1.052	1.110
393.40	0.2730	0.1682	1.235	1.028	399.34	0.5759	0.3554	1.035	1.125
393.75	0.2922	0.1798	1.220	1.029	400.81	0.6231	0.3956	1.020	1.133
394.06	0.3139	0.1902	1.190	1.038	402.58	0.6799	0.4451	1.000	1.159
394.07	0.3143	0.1910	1.193	1.037	404.76	0.7427	0.5096	0.985	1.191
394.44	0.3373	0.2032	1.169	1.044	407.31	0.8062	0.5864	0.972	1.234
394.79	0.3560	0.2146	1.158	1.047	409.72	0.8589	0.6659	0.969	1.274
394.84	0.3566	0.2149	1.156	1.045	412.38	0.9115	0.7665	0.977	1.313
395.26	0.3856	0.2289	1.124	1.061	415.49	0.9618	0.8890	0.989	1.322
				Butyl Butanoate (1) + 1-Butanol (2)					
390.79	0.0266	0.0104	1.536	0.997	400.29	0.4446	0.1678	1.086	1.076
390.87	0.0344	0.0130	1.476	1.000	401.62	0.4828	0.1865	1.066	1.082
391.49	0.0687	0.0251	1.398	1.003	403.08	0.5233	0.2077	1.047	1.093
392.04	0.1002	0.0361	1.352	1.007	404.81	0.5619	0.2314	1.030	1.093
392.66	0.1323	0.0472	1.312	1.011	406.88	0.6107	0.2633	1.013	1.106
393.29	0.1642	0.0577	1.267	1.017	408.58	0.6465	0.2913	1.006	1.113
394.05	0.2008	0.0703	1.232	1.023	410.67	0.6869	0.3257	0.995	1.124
394.76	0.2426	0.0825	1.168	1.040	413.25	0.7261	0.3682	0.987	1.116
395.93	0.2891	0.1010	1.155	1.045	416.15	0.7687	0.4174	0.973	1.120
396.86	0.3283	0.1151	1.125	1.056	419.38	0.8121	0.4741	0.955	1.136
398.29	0.3796	0.1384	1.117	1.063	423.23	0.8576	0.5545	0.952	1.143
398.45	0.3904	0.1414	1.104	1.072	426.80	0.8958	0.6396	0.955	1.148
399.36	0.4160	0.1544	1.100	1.071	431.30	0.9375	0.7564	0.959	1.150
400.21	0.4426	0.1668	1.087	1.076	434.81	0.9660	0.8547	0.962	1.153

ethanoate (1) + 1-butanol (2) show azeotropes. Suitable VLE correlations were used to calculate the coordinates of the singular point, and the results are shown and compared with those reported by other researchers in Table 5. There were no significant differences when the azeotropes were calculated by interpolation from the plots of the curves.

Comparative Analysis of the VLE Data. Figure 5 presents comparisons of the plots of $y_1 - x_1$ versus x_1 for the data contained in Table 3 together with the corresponding experimental values and correlations compiled from the literature for the mixture of butyl ethanoate (1) + 1-butanol (2); Figure 6 does the same for the mixture of butyl butanoate (1) + 1-butanol (2). The literature values for the former mixture were consistent using the test proposed by Fredenslund et al. (1977b), with the exception of the values reported by Beregovykh et al. (1971), which displayed appreciable differences from our values. Thus, at $x_1 = 0.8$ the difference observed for y_1 was $\delta(y_1) = 0.050$. The mean discrepancy between the values published by Brunjes and Furnas (1935) and Sheinker and Peresleni (1952) was also substantial, at $\bar{\delta}(y_1) = 0.011$. The mean discrepancies with respect to the other literature values were similar. The literature values that were most consistent both with other literature values and with the

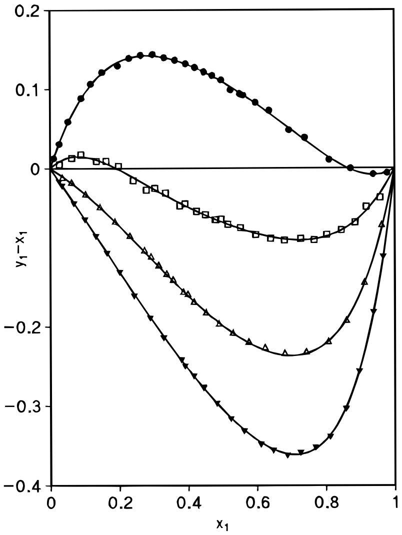

Figure 3. Representation of $y_1 - x_1$ *vs* x_1 for the mixtures butyl esters (1) + 1-butanol (2): (●) methanoate; (□) ethanoate; (△) propanoate; (▼) butanoate.

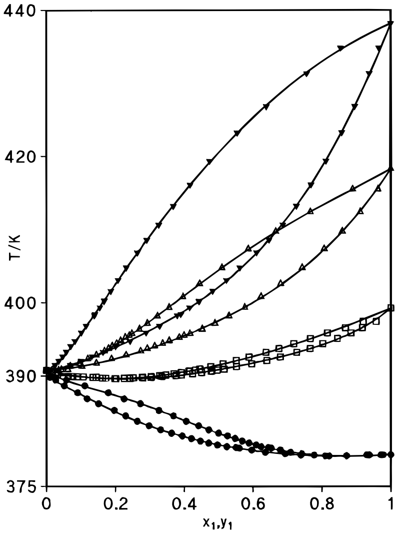

Figure 4. Representation of T *vs* x_1 or y_1 for the mixtures butyl esters (1) + 1-butanol (2): (●) methanoate; (□) ethanoate; (△) propanoate; (▼) butanoate.

Table 4. Parameters Obtained for Eqs 4 and 5 and Standard Deviations, *s*, of the Differents Correlations

correlation	k	A_0	A_1	A_2	A_3	s
			Butyl Methanoate (1) + 1-Butanol (2)			
$y_1 - x_1$ *vs* x_1	1.078	1.323	−3.245	4.115	−2.490	0.002
T *vs* x_1	0.09	−87.40	254.01	−338.04	157.17	0.07
T *vs* y_1	0.56	−21.10	94.50	−188.35	101.30	0.08
			Butyl Ethanoate (1) + 1-Butanol (2)			
$y_1 - x_1$ *vs* x_1	0.792	0.425	−2.569	3.711	−2.417	0.003
T *vs* x_1	1.91	−19.56	19.38	−30.98		0.12
T *vs* y_1	0.06	−94.42	304.71	−417.88	196.32	0.08
			Butyl Propanoate (1) + 1-Butanol (2)			
$y_1 - x_1$ *vs* x_1	1.751	−0.260	−1.707	1.211	−1.541	0.001
T *vs* x_1	0.87	−25.54	12.26	−31.03		0.11
T *vs* y_1	0.90	−25.76	71.88	−44.68		0.06
			Butyl Butanoate (1) + Butanol (2)			
$y_1 - x_1$ *vs* x_1	1.824	−0.618	−1.696	0.804	−2.272	0.001
T *vs* x_1	0.50	−42.72	29.75	−59.62		0.17
T *vs* y_1	0.18	−28.62	98.70	−42.96		0.12

Table 5. Azeotropes Obtained for the Systems Butyl Methanoate (1) + 1-Butanol (2) and Butyl Ethanoate (1) + 1-Butanol (2)

$x_1 = y_1$	T/K	ref
	Butyl Methanoate + 1-Butanol	
0.871	379.14	this work
0.701	378.95	Horsley (1952)
	Butyl Ethanoate + 1-Butanol	
0.222	389.64	this work
0.230	389.97	Beregovykh et al. (1971)[a]
0.271	389.35	Brunjes and Furnas (1935)[b]
0.206	390.25	Figurski and von Weber (1977)
0.257	390.00	Mato and Cepeda (1985)
0.235	389.55	Ortega et al. (1987)
0.194	389.95	Sheinker and Peresleni (1952)[b]
0.237	390.75	Horsley (1952)

[a] See Gmehling et al. (1982). [b] See Gmehling et al. (1978).

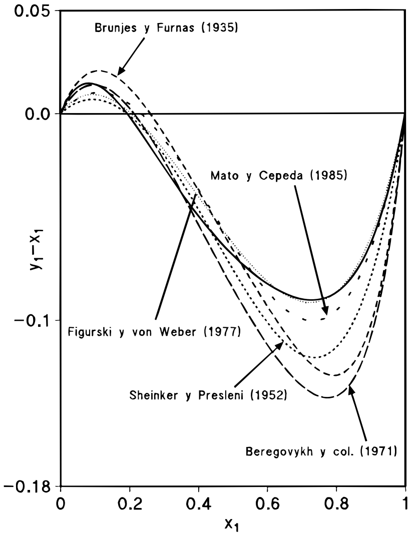

Figure 5. Comparison of our (—) experimental curve $y_1 - x_1$ *vs* x_1 for butyl ethanoate (1) + 1-butanol (2) with those presented in the literature.

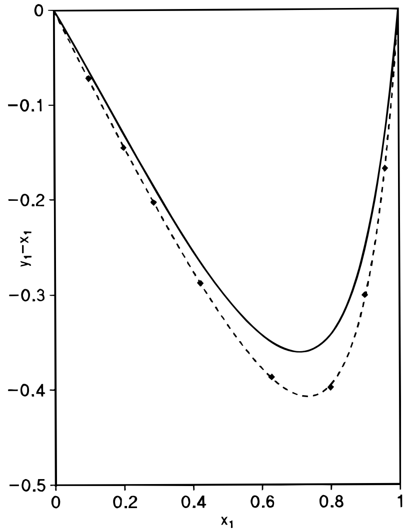

Figure 6. Comparison of our (—) experimental curve $y_1 - x_1$ *vs* x_1 for butyl butanoate (1) + 1-butanol (2) with that from Volkova et al. (1979) (- - -).

values presented here were those of Figurski and von Weber (1977), Mato and Cepeda (1985), and Ortega et al. (1987), with an overall mean error of $\bar{\delta}(y_1) = 0.004$. For the latter mixture, the only VLE values found at the same pressure were those reported by Volkova et al. (1979), which presented a negative consistency using the same test, with a maximum discrepancy for the vapor-phase composition value of 0.055 as compared to the experimental data given in Table 3 (see Figure 6).

Table 6. Mean Deviation $\bar{\delta}(y_1)$ and Average Percent Errors $\bar{e}(\gamma_i)$ Obtained in the Prediction of VLE Using Different Group-Contribution Models[a]

	ASOG	UNIFAC					modified UNIFAC		
	OH/COO[b]	OH/HCOO[c]	OH/COOC[c]	COH/COO[d]	CCOH/COOC[e]	OH/COO[f]	OH/COOC[g]	OH/HCOO[h]	OH/COOC[h]
Butyl Methanoate (1) + 1-Butanol (2)									
$\bar{e}(\gamma_i)$	3.5	10.2		6.1		2.8		4.4	
$\bar{\delta}(y_1)$	0.016	0.025		0.013		0.011		0.009	
$\delta_{\max}(y_1)$	0.035	−0.062		−0.034		0.028		−0.021	
(at x_1 =)	(0.636)	(0.197)		(0.197)		(0.636)		(0.197)	
Butyl Ethanoate (1) + 1-Butanol (2)									
$\bar{e}(\gamma_i)$	3.9		10.7	12.0	7.1	6.0	1.3		1.6
$\bar{\delta}(y_1)$	0.010		0.027	0.032	0.018	0.015	0.007		0.007
$\delta_{\max}(y_1)$	−0.024		−0.054	−0.060	−0.038	−0.034	0.020		0.020
(at x_1 =)	(0.279)		(0.279)	(0.279)	(0.279)	(0.279)	(0.917)		(0.917)
Butyl Propanoate (1) + 1-Butanol (2)									
$\bar{e}(\gamma_i)$	4.8		15.5	14.3	12.8	9.0	3.7		5.1
$\bar{\delta}(y_1)$	0.009		0.032	0.030	0.027	0.018	0.009		0.011
$\delta_{\max}(y_1)$	−0.018		−0.042	−0.039	−0.035	−0.023	−0.019		−0.020
(at x_1 =)	(0.859)		(0.386)	(0.386)	(0.386)	(0.386)	(0.859)		(0.806)
Butyl Butanoate (1) + 1-Butanol (2)									
$\bar{e}(\gamma_i)$	7.2		21.9	19.1	18.5	14.2	6.6		7.0
$\bar{\delta}(y_1)$	0.010		0.025	0.023	0.022	0.017	0.011		0.011
$\delta_{\max}(y_1)$	−0.025		−0.032	−0.030	−0.029	−0.028	−0.025		−0.025
(at x_1 =)	(0.858)		(0.328)	(0.858)	(0.858)	(0.858)	(0.896)		(0.858)

[a] $\bar{e}(\gamma_i) = \sum_{i=1}^{2}\sum_{N=1}^{N}|(\gamma_{i,\mathrm{exp}} - \gamma_{i,\mathrm{cal}})/\gamma_{i,\mathrm{exp}}| \times 100/N$; $\bar{\delta}(y_1) = \sum_{N=1}^{N}|y_{1,\mathrm{exp}} - y_{1,\mathrm{cal}}|/N$; $\delta_{\max}(y_1) = y_{1,\mathrm{exp}} - y_{1,\mathrm{cal}}$. [b] Kojima and Tochigi (1979). [c] Hansen et al. (1991). [d] Fredenslund et al. (1975). [e] Fredenslund et al. (1977a). [f] Macedo et al. (1983). [g] Larsen et al. (1987). [h] Gmehling et al. (1993).

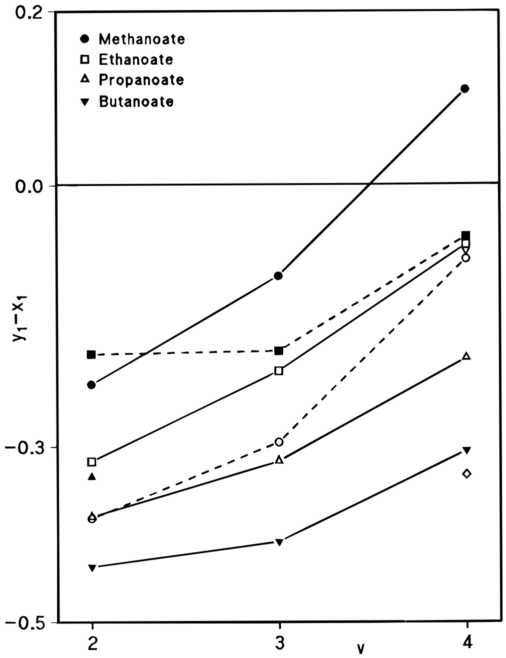

Figure 7. Variation of $y_1 - x_1$ for the mixtures butyl esters (1) $C_vH_{2v+1}(OH)$ (v = 2−4) (2) as a function of alcohol chain length. Comparison of our experimental values with those from the literature: (◇) Volkova et al. (1979); (○) Beregovykh et al. (1971); (■) Ortega et al. (1987); (▲) Shono and Kanazawa (1969); (▽) Sheinker and Peresleni (1952).

According to the values for the mixture of butyl methanoate (1) + 1-butanol (2) shown in Table 5, the difference in the value for the azeotrope calculated here and the value proposed by Horsley (1952) was rather substantial. On the other hand, the discrepancy was smaller for the mixture of butyl ethanoate (1) + 1-butanol (2), for which the coordinates of the azeotrope were closer together. Omitting the extreme values from the values listed in Table 5, the mean value was rather close to the value presented here.

This paper is one of a series of papers concerned with the systematic study of isobaric VLEs of mixtures of butyl esters (1) + 1-alcohols (2) under way in our laboratory, and Figure 7 graphically presents a compilation of the experimental values obtained for such mixtures to date, plotting the sequence of equimolar values for $y_1 - x_1$ versus 1-alcohol chain length. The figure depicts a quasi-regular increase in the value of the said magnitude and the discrepancies between those values and the literature values.

Prediction of VLEs Using Group-Contribution Models. The following group-contribution models were employed: the ASOG model (Kojima and Tochigi, 1979), the UNIFAC model (Fredenslund et al., 1975), and the modified versions of the UNIFAC model proposed by Larsen et al. (1987) and Gmehling et al. (1993). For all cases, the activity coefficients, γ_i, and the composition of the vapor phase, y_1, obtained experimentally were compared with the theoretical predictions. Table 6 presents a quantitative appraisal of the theoretical estimates achieved. The version of the UNIFAC model proposed by Larsen et al. (1987) yielded the best predictions for γ_i; this version could not be applied for the mixture of butyl methanoate + 1-butanol, because no values were available for the interaction pair OH/HCOO. This modified version of the UNIFAC model yielded a mean error of 4% for the estimates of γ_i for the other three mixtures. The ASOG model and the other modified version of the UNIFAC model proposed by Gmehling et al. (1993) likewise produced excellent results, with mean errors of less than 5% for the four systems. The original UNIFAC model as proposed by Fredenslund et al. (1975) yielded a higher mean error for the γ_i values, 8% using the values for the interaction pair OH/COO published by Macedo et al. (1983) and recommended for non-alkyl esters and 14% using the values for the alcohol/ester interaction published by Hansen et al. (1991).

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