Densities and Isobaric Vapor–Liquid Equilibria of Butyl Esters (Methanoate to Butanoate) with Ethanol at 101.32 kPa

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Vapor–liquid equilibrium and densities at 101.32 kPa have been determined for the binary systems formed by four butyl esters (from methanoate to butanoate) with ethanol. The four systems exhibit positive deviations from ideal behavior, and all data (p–T–x–y) were found to be thermodynamically consistent. The activity coefficients and the dimensionless function G^E/RT of the solution were correlated with its concentration by different equations. An azeotrope was found in the mixture butyl methanoate (1) + ethanol (2) at T = 350.9 K and $x_1 = y_1$ = 0.088. The group contribution models ASOG and modified UNIFAC gave fair predictions.

Introduction

Our research team has been conducting a program of experimental measurements for binary mixtures containing methyl esters (Ortega et al., 1990), ethyl esters (Ortega et al., 1986), and propyl esters (Ortega and Galván, 1994) under a research project designed to study the vapor–liquid equilibria (VLE) of binary mixtures of alkyl esters and alcohols. In the framework of that study, the present contribution gives experimental VLE results for binary mixtures consisting of butyl esters (from methanoate to butanoate) and ethanol at a constant pressure of 101.32 kPa. The literature consulted has disclosed values for the binary mixture butyl ethanoate + ethanol [Beregovykh, V. V.; Timofeev, V. S.; Lukyanova, R. N. *Uch. Zap. Mosk. Inst. Tonkoi Khim. Tekhnol.* **1971**, *1*, 38. Shono, H.; Kanazawa, N. *Kogyo Kagaku Zasshi* **1969**, *72*, 815 (see Gmehling et al. (1988) and Ortega et al. (1987))]. Now in our laboratory new equipment exists that gives more precise VLE data; therefore, for that system new measurements were made in oder to present a comprehensive analysis of mixtures of the first butyl esters and normal and isomeric alcohols.

The present paper also considers the applicability of group contribution methods to such mixtures, in particular the ASOG model (Tochigi et al., 1990) and three versions of the UNIFAC model, the original model put forth by Fredenslund et al. (1975) and the modified versions put forth by Larsen et al. (1986) and by Weidlich and Gmehling (1987).

Experimental Section

Chemicals. All the components used in this study (butyl methanoate, 97 + mol %, and propanoate, 99 + mol%, from Aldrich and butyl ethanoate and butanoate, >99 mol %, and ethanol, >99.8 mol %, from Fluka) were of the highest commercial grade, and all were degassed using ultrasound and dried on molecular sieves (type 3Å from Fluka) before use. The main physical properties were determined for each of the components experimentally, and results are shown together with literature values in Table 1. There was an unexplained discrepancy in the values of n(D,298.15 K) and $T_{b,i}$ for butyl propanoate.

Table 1. Densities, ϱ, Refractive Indices, n(D), and Normal Boiling Points, T_b, of the Chemicals Used in This Study

	ϱ(298.15 K)/ (kg·m^{-3})		n(D, 298.15 K)		T_b/K	
	exptl	lit.	exptl	lit.	exptl	lit.
butyl methanoate	887.64	886.9^{a,b}	1.3872	1.3874^{a,b}	379.30	379.25^{a,b}
butyl ethanoate	875.89	876.36^{a} 876.6^{b}	1.3920	1.3918^{a,b}	399.26	399.21^{a} 399.15^{b}
butyl propanoate	871.12	871.4^{b}	1.3989	1.4000^{b}	418.26	419.75^{b}
butyl butanoate	864.67	866.4^{b}	1.4040	1.4029^{b}	438.15	438.15^{b}
ethanol	785.38	784.93^{a} 785.09^{b}	1.3595	1.35941^{a,b}	351.45	351.44^{a,b}

[a] Riddick et al. (1986). [b] TRC (1993).

Equipment and Procedure. The ebulliometer employed in the present study was small (≈60 cm^3), and the two phases were refluxed. A detailed description of the equipment and operating methods employed has already been published elsewhere (Ortega et al., 1986; Ortega and Susial, 1991).

The composition of the vapor and liquid phases was calculated indirectly from density, ϱ, values using an Anton Parr Model DMA-55 densimeter calibrated using water and n-nonane (Ortega et al., 1985) to a precision of ±0.02 kg·m^{-3}. The phase compositions were established from the respective correlations for V^E on x, x being the butyl ester concentration. The values obtained did not differ significantly from the values based on correlations of the type $\varrho = \varrho(x)$.

Experimental Results

Densities. The excess volumes for each binary system (butyl ester (1) + ethanol (2)) were calculated from measured densities, at known concentrations at 298.15 K. The precision of the estimates was $\pm 10^{-4}$ for mole fraction, ±0.02 K for temperature measurements, and $\pm 2 \times 10^{-9}$ m^3·mol^{-1} for V^E. Table 2 presents the density and V^E values. The experimental excess volumes were correlated

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Table 2. Densities and Excess Volumes at 298.15 K for Butyl Esters (1) + Ethanol (2)

x_1	$\varrho/(\mathrm{kg{\cdot}m^{-3}})$	$10^9V^E/(\mathrm{m^3{\cdot}mol^{-1}})$	x_1	$\varrho/(\mathrm{kg{\cdot}m^{-3}})$	$10^9V^E/(\mathrm{m^3{\cdot}mol^{-1}})$
		Butyl Methanoate (1) + Ethanol (2)			
0.0242	790.61	−16	0.5213	854.50	65
0.0716	799.35	−22	0.5536	857.31	66
0.1043	804.56	7	0.6196	862.70	69
0.1426	810.53	18	0.7615	873.06	63
0.2076	819.94	30	0.8284	877.43	57
0.2724	828.41	39	0.8931	881.41	45
0.3555	838.11	52	0.9431	884.40	25
0.4740	850.18	63			
		Butyl Ethanoate (1) + Ethanol (2)			
0.0343	791.89	17	0.4542	843.35	123
0.0720	798.56	26	0.5118	847.89	130
0.1128	805.03	46	0.5693	852.05	135
0.1537	810.97	65	0.6861	859.63	130
0.2078	818.20	79	0.7607	863.99	112
0.2639	824.94	91	0.8590	869.13	89
0.3043	829.38	98	0.9446	873.31	43
0.3432	833.32	109			
		Butyl Propanoate (1) + Ethanol (2)			
0.0511	795.27	20	0.4511	842.39	110
0.1031	804.21	34	0.4801	844.55	112
0.1464	810.71	50	0.5777	851.07	114
0.1872	816.25	62	0.6921	857.55	111
0.2468	823.51	74	0.7826	862.00	100
0.3033	829.51	87	0.8284	864.07	90
0.3481	833.82	94	0.9295	868.39	40
0.4023	838.52	104			
		Butyl Butanoate (1) + Ethanol (2)			
0.0593	796.87	26	0.4671	840.91	126
0.1087	805.02	49	0.5948	848.37	133
0.1603	812.37	67	0.6795	852.51	129
0.2055	818.03	77	0.7108	853.90	128
0.2603	824.00	93	0.7482	855.51	120
0.3102	828.81	104	0.8456	859.33	94
0.3504	832.29	112	0.8938	861.07	74
0.3961	835.93	116	0.9265	862.27	44

Table 3. Coefficients *k* and A_i in Eq 1 and Standard Deviations, $s(V^E)$

mixture	k	A_0	A_1	A_2	A_3	$10^9s(V^E)/(\mathrm{m^3{\cdot}mol^{-1}})$
butyl methanoate (1) + ethanol (2)	0.23	−1449	7554	−11514	5900	4
butyl ethanoate (1) + ethanol (2)	1.44	472	−96	503		3
butyl propanoate (1) + ethanol (2)	1.21	398	−56	398		2
butyl butanoate (1) + ethanol (2)	0.89	537	−396	684		3

by means of the equation

$$10^9V^E/(\mathrm{m^3{\cdot}mol^{-1}}) = x_1x_2\sum A_i(x_1/[x_1 + kx_2])^i \qquad (1)$$

The values of the coefficients A_i and k were calculated using the method of least squares, and the corresponding coefficient values and standard deviations, $s(V^E)$, for each system are given in Table 3. The only V^E values for these systems were those published in earlier work carried out in this same series, for butyl methanoate + ethanol (Ortega, 1985) and butyl ethanoate + ethanol (Ortega et al., 1985). With respect to the curves presented in this paper the differences in V^E were minimal, less than 4×10^{-9} m³·mol⁻¹ for the two cases.

Table 4. Experimental Vapor Pressures, $p°_i$, of Butyl Esters as a Function of Temperature, *T*

T/K	$p°_1$/kPa	T/K	$p°_1$/kPa	T/K	$p°_1$/kPa
		Butyl Methanoate			
362.88	59.04	373.77	84.88	383.65	115.65
363.53	60.43	374.82	87.75	384.24	117.85
364.45	62.30	375.56	90.02	385.27	121.58
365.33	64.25	376.51	92.73	385.95	124.07
366.12	65.85	377.17	94.63	386.99	128.16
366.89	67.67	377.93	96.82	387.80	131.31
367.55	69.18	378.91	99.95	388.57	134.07
368.83	72.21	379.67	102.29	389.37	137.60
369.56	73.98	380.49	105.01	389.55	138.19
370.75	76.93	381.20	107.40	390.74	143.00
372.15	80.61	381.99	110.03	392.35	150.16
373.03	82.87	382.73	112.59		
		Butyl Ethanoate			
382.06	60.64	393.63	86.34	402.86	112.56
383.80	64.06	394.43	88.39	403.51	114.65
384.36	65.15	395.26	90.58	404.10	116.43
385.07	66.60	395.89	92.26	404.92	119.21
386.33	69.27	396.69	94.38	405.49	121.07
387.30	71.34	397.46	96.54	406.07	123.08
388.07	73.06	398.34	99.07	406.65	125.27
389.19	75.60	399.09	101.24	407.11	126.74
390.18	77.90	399.82	103.31	407.75	129.02
391.01	79.85	400.42	105.15	408.44	131.44
391.61	81.32	401.13	106.95	409.34	134.64
392.33	83.08	401.90	109.62	410.04	136.98
392.90	84.50	402.38	111.01		
		Butyl Propanoate			
403.00	65.82	414.14	90.86	423.78	118.37
403.77	67.30	414.79	92.62	424.34	120.18
404.54	68.88	415.42	94.12	424.91	121.97
405.22	70.31	416.02	95.69	425.32	123.30
406.10	72.12	416.71	97.52	425.95	125.23
407.06	74.20	417.43	99.49	426.46	126.95
407.42	74.99	418.05	101.17	427.68	131.16
408.10	76.53	418.48	102.49	428.05	132.49
409.06	78.65	419.15	104.31	428.54	134.27
410.17	81.22	419.75	106.17	429.09	136.19
410.66	82.37	420.26	107.60	429.84	138.81
411.32	83.92	421.01	109.72	430.24	140.36
412.08	85.73	421.88	112.46	430.81	142.45
412.76	87.43	422.19	113.41	431.46	144.86
413.46	89.16	422.94	115.71		
		Butyl Butanoate			
425.06	71.00	434.29	91.52	443.64	116.62
425.93	72.73	434.97	93.26	444.13	118.11
426.66	74.27	435.54	94.68	444.83	120.10
427.42	75.84	436.23	96.35	445.19	121.28
428.05	77.15	437.00	98.30	445.77	123.05
428.96	79.11	437.65	99.94	446.31	124.70
429.59	80.44	438.30	101.65	446.92	126.64
430.17	81.75	438.79	103.10	447.39	128.07
430.71	83.07	439.65	105.42	448.03	130.20
431.25	84.24	440.20	106.94	448.80	132.72
431.99	85.99	440.99	109.12	449.34	134.50
432.53	87.25	441.54	110.70	449.81	136.06
433.08	88.62	442.38	113.01		
433.67	90.04	443.19	115.22		

Vapor Pressures. Vapor pressures for pure liquids are required in the treatment of VLE data, with a bearing both on the activity coefficients and on the thermodynamic validation of the mixture results. It was therefore decided to make new measurements of the vapor pressure for each of the butyl esters; more recent measurements of those values were available for ethanol (Ortega et al., 1990). These values appear in Table 4. The experimental values were correlated by means of the Antoine equation using a nonlinear regression procedure. The values of the constants *A*, *B*, and *C* are shown in Table 5 together with the literature values. The deviations, $\delta(p°_i)$, calculated by means of the Antoine equation using the constant values from Table 5 and from the literature have been graphically represented in Figures 1−3. For butyl methanoate the mean error was less than 1% with respect to the TRC (1993) values and less than 2% with respect to the values

Table 5. Coefficients A, B, and C of the Antoine Equation,[a] Range of Temperature, and Standard Deviations, $s(p°_i)$, from This Work and from the Literature

	A	B	C	T/K range	$s(p°_i)$/kPa	ref
butyl methanoate	6.70820	1627.85	33.17	350−400	0.08	this work
	6.81853	1698.73	25.74	300−385	0.42	*b*
	6.5277	1533.4	40.2			*c*, *d*
butyl ethanoate	6.44352	1584.05	42.20	350−450	0.08	this work
	6.25202	1430.42	62.40	330−400	0.04	*b*
	6.151445	1368.05	69.22			*c*
	6.5000	1596.7	43.85			*d*
butyl propanoate	6.57595	1745.90	36.04	350−450	0.07	this work
	8.60979	2852.58	−23.83	305−365	0.08	*b*
butyl butanoate	6.13153	1500.71	74.43	400−450	0.07	this work
	7.27661	2309.44	0.00	325−435		*e*
ethanol	7.1130	1513.02	55.15			*f*

[a] $\log(p°_i/\text{kPa}) = A - B/[(T/\text{K}) - C]$. [b] Boublick et al. (1973). [c] Riddick et al. (1986). [d] TRC (1993). [e] Gmehling et al. (1988). [f] Ortega et al. (1990).

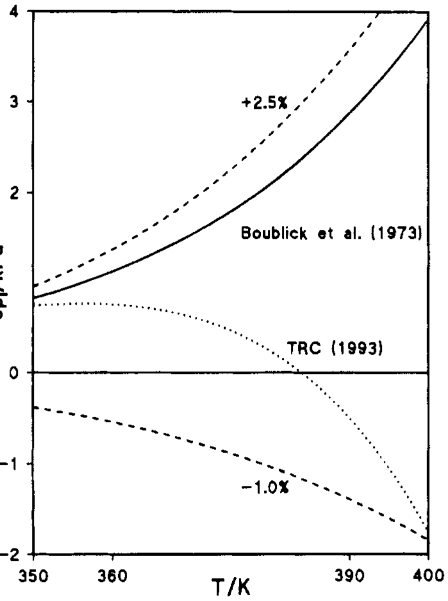

Figure 1. Differences, $\delta p°_i = p°_{i,\text{bib}} - p°_{i,\text{exp}}$, obtained for vapor pressures of butyl methanoate using the Antoine equation and the constants from the literature indicated.

reported by Boublick et al. (1973) over the same temperature range. For butyl ethanoate the mean difference was likewise 1.5% as compared to TRC (1993) values and 1.2% with respect to the curve reported by Boublick et al. (1973) and Riddick et al. (1986). For butyl butanoate the difference between the vapor pressures and those used by Gmehling et al. (1988) was 2%. It was not possible to compare the values for butyl propanoate with those published by Boublick et al. (1973), because the temperature ranges used were different.

Vapor−Liquid Equilibrium Data. Table 6 presents the p, T, x, and y results at (101.32 ± 0.02) kPa for the mixtures considered in this study. The table also lists activity coefficient values for the liquid phase calculated using

$$\gamma_i = (\phi_i y_i p/(x_i \phi°_i p°_i)) \exp[(p°_i - p)v_i^{\text{L}}/RT] \qquad (2)$$

The fugacity coefficient, ϕ_i and $\phi°_i$, values were calculated using a virial equation truncated at the second term:

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

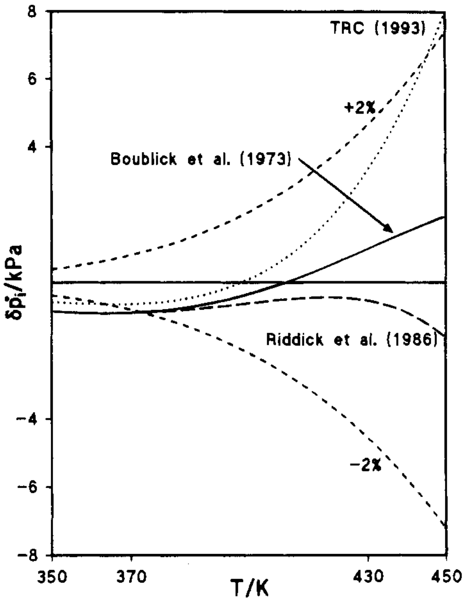

Figure 2. Differences, $\delta p°_i = p°_{i,\text{bib}} - p°_{i,\text{exp}}$, obtained for vapor pressures of butyl ethanoate using the Antoine equation and the constants from the literature indicated.

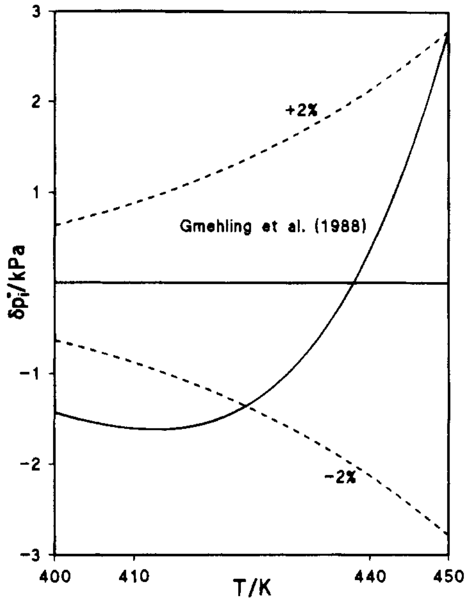

Figure 3. Differences, $\delta p°_i = p°_{i,\text{bib}} - p°_{i,\text{exp}}$, obtained for vapor pressures of butyl butanoate, and using the Antoine equation and the constants from the literature indicated.

The second virial coefficients for the pure components and the mixtures were calculated using Tsonopoulos' empirical equation (1974). The molar volume, v_i^{L}, and its variation with temperature were estimated using a modified version of Rackett's equation (Spencer and Danner, 1972). The thermodynamic consistency of the data was verified using the point-to-point test of Van Ness et al. (1973) (Fredenslund et al., 1977), calculating the virial coefficients as explained above. All the systems were consistent for the relationship $|\delta y_1| < 0.01$ used by the method.

The experimental results were correlated using the following polynomial equation

$$Q = x_1 x_2 \sum A_i (x_1/(x_1 + kx_2))^i \qquad (4)$$

fitting the values of $Q = y_1 - x_1$ and G^{E}/RT against ester composition, x_1. An equation similar to the equation similar to the equation proposed by Wisniak and Tamir

Table 6. Experimental VLE Data at 101.32 kPa for Butyl Esters (1) + Ethanol (2)

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
Butyl Methanoate (1) + Ethanol (2)									
351.07	0.0108	0.0185	4.280	0.994	355.52	0.6141	0.3292	1.152	1.476
351.00	0.0422	0.0505	3.008	0.995	356.24	0.6267	0.3379	1.130	1.467
350.97	0.0643	0.0670	2.624	1.002	356.60	0.6437	0.3483	1.120	1.494
351.00	0.0975	0.0945	2.439	1.007	357.45	0.6903	0.3698	1.077	1.611
351.05	0.1320	0.1171	2.229	1.019	358.55	0.7189	0.3953	1.065	1.638
351.09	0.1895	0.1312	1.737	1.073	361.01	0.7893	0.4538	1.025	1.810
351.14	0.2044	0.1455	1.782	1.073	362.27	0.8091	0.4829	1.020	1.809
351.45	0.2749	0.1725	1.555	1.126	364.07	0.8462	0.5286	1.007	1.924
351.57	0.2984	0.1821	1.505	1.146	365.10	0.8603	0.5555	1.006	1.928
352.30	0.3957	0.2235	1.358	1.229	367.82	0.8935	0.6275	1.002	1.935
352.69	0.4343	0.2396	1.308	1.267	369.93	0.9114	0.6733	0.986	1.904
353.53	0.5060	0.2686	1.222	1.352	371.25	0.9232	0.7071	0.980	1.885
353.87	0.5228	0.2795	1.216	1.362	372.57	0.9322	0.7458	0.983	1.775
354.27	0.5435	0.2931	1.210	1.377	375.67	0.9655	0.8498	0.983	1.871
354.85	0.5845	0.3097	1.165	1.446	377.47	0.9764	0.9111	0.987	1.528
Butyl Ethanoate (1) + Ethanol (2)									
352.32	0.0856	0.0492	2.514	0.994	364.12	0.6324	0.2408	1.102	1.294
353.16	0.1437	0.0685	2.022	1.007	365.70	0.6716	0.2622	1.072	1.334
354.21	0.2121	0.0936	1.803	1.025	366.82	0.6963	0.2770	1.052	1.361
355.12	0.2664	0.1091	1.620	1.046	368.25	0.7244	0.2971	1.035	1.391
356.52	0.3439	0.1310	1.433	1.085	370.52	0.7631	0.3302	1.014	1.430
357.42	0.3897	0.1462	1.368	1.109	372.77	0.7957	0.3645	0.998	1.463
358.37	0.4340	0.1608	1.306	1.136	376.04	0.8353	0.4183	0.984	1.497
359.04	0.4626	0.1701	1.267	1.155	378.76	0.8627	0.4671	0.977	1.512
359.76	0.4920	0.1801	1.230	1.177	383.05	0.8987	0.5516	0.972	1.514
360.58	0.5231	0.1912	1.194	1.202	386.12	0.9205	0.6171	0.969	1.505
361.62	0.5589	0.2063	1.163	1.229	389.68	0.9430	0.6998	0.967	1.486
362.32	0.5813	0.2167	1.147	1.247	394.31	0.9703	0.8279	0.975	1.436
362.97	0.6010	0.2254	1.128	1.266					
Butyl Propanoate (1) + Ethanol (2)									
351.50	0.0137	0.0046	2.820	0.994	367.52	0.5732	0.1493	1.211	1.113
351.63	0.0417	0.0117	2.339	1.011	369.61	0.6114	0.1662	1.175	1.118
352.32	0.0744	0.0195	2.126	1.012	371.25	0.6431	0.1807	1.147	1.134
352.88	0.1037	0.0257	1.970	1.017	373.16	0.6725	0.1948	1.108	1.142
353.11	0.1203	0.0305	2.000	1.022	377.29	0.7273	0.2350	1.076	1.143
353.89	0.1530	0.0373	1.863	1.025	381.00	0.7688	0.2713	1.041	1.146
354.53	0.1877	0.0442	1.757	1.036	383.31	0.7903	0.2971	1.029	1.137
355.28	0.2264	0.0510	1.635	1.051	387.03	0.8254	0.3439	1.014	1.143
356.25	0.2652	0.0592	1.561	1.059	391.01	0.8558	0.3942	0.991	1.140
357.55	0.3156	0.0697	1.471	1.073	395.00	0.8828	0.4479	0.967	1.144
358.94	0.3590	0.0804	1.417	1.077	401.05	0.9173	0.5424	0.943	1.143
361.35	0.4255	0.0992	1.351	1.081	405.73	0.9409	0.6321	0.938	1.140
365.50	0.5316	0.1333	1.251	1.106	411.70	0.9702	0.7857	0.959	1.137
Butyl Butanoate (1) + Ethanol (2)									
351.48	0.0188	0.0033	3.001	1.002	364.42	0.4637	0.0591	1.292	1.088
352.27	0.0482	0.0084	2.910	0.997	365.10	0.4853	0.0617	1.254	1.105
353.01	0.0946	0.0129	2.193	1.015	366.16	0.5172	0.0659	1.208	1.131
353.35	0.1175	0.0151	2.045	1.026	368.30	0.5705	0.0745	1.140	1.173
354.47	0.1462	0.0190	1.974	1.014	370.09	0.6390	0.0813	1.037	1.305
355.18	0.1696	0.0221	1.922	1.012	372.95	0.6969	0.0926	0.973	1.400
355.93	0.1985	0.0250	1.799	1.018	375.94	0.7349	0.1062	0.948	1.433
357.04	0.2290	0.0297	1.767	1.011	379.51	0.7738	0.1233	0.919	1.474
358.30	0.2762	0.0346	1.623	1.025	384.34	0.8131	0.1518	0.909	1.493
360.07	0.3265	0.0429	1.586	1.025	395.45	0.8729	0.2380	0.915	1.437
360.15	0.3472	0.0433	1.500	1.054	400.80	0.8916	0.2853	0.906	1.369
361.30	0.3753	0.0475	1.453	1.053	414.45	0.9374	0.4521	0.907	1.291
363.04	0.4218	0.0539	1.369	1.064	425.50	0.9657	0.6327	0.907	1.228

(1976) was used to correlate temperature and the mole fractions for the liquid and vapor phases, such that

$$T = \sum x_1 T^{\circ}_{i,b} + Q \qquad (5)$$

where Q is defined as in eq 4 and $T^{\circ}_{i,\mathrm{b}}$ is the boiling temperature of pure component i at the working pressure.

Table 7 lists the values of the coefficients in eq 4 with the corresponding standard deviations, $s(Q)$, for the respective correlations.

Figures 4 and 5 plot the experimental values and the fitted curves for the different systems studied. Figure 6 compares the data in Table 6 with the literature values for the system butyl ethanoate + ethanol. The test by Fredenslund et al. (1977) applied to the VLE data from the literature in Figure 6 showed that in all cases the data are not consistent. The values presented here differed significantly from the values reported by Beregovykh et al. (*Uch. Zap. Mosk. Inst. Tonkoi Khim. Technol.* **1971**, *1*, 38); however, they displayed rather good agreement with the values reported by Shono and Kanazawa (*Kogyo Kagaku Zasshi* **1969**, *72*, 815). With respect to our previous values (Ortega et al., 1987) the main difference

Table 7. Coefficients A_i and k in Eq 4 and Standard Deviations, $s(Q)$, Obtained by Correlating the Different Functions

function	k	A_0	A_1	A_2	A_3	$s(Q)$
Butyl Methanoate (1) + Ethanol (2)						
$y_1 - x_1$ vs x_1	0.928	0.444	−5.630	10.578	−9.192	0.005
T vs x_1	1.019	−39.160	28.113	−89.288		0.38
T vs y_1	0.200	−26.464	−69.046	106.001		0.16
Butyl Ethanoate (1) + Ethanol (2)						
$y_1 - x_1$ vs x_1	1.635	−0.293	−3.524	5.199	−7.047	0.001
T vs x_1	1.290	−41.792	3.595	−111.371		0.17
T vs y_1	0.213	−45.451	41.616	151.404	−126.463	0.08
Butyl Propanoate (1) + Ethanol (2)						
$y_1 - x_1$ vs x_1	3.299	−0.729	−3.276	0.484	−4.242	0.002
T vs x_1	1.292	−59.583	−2.525	−117.750		0.18
T vs y_1	0.148	−58.741	310.908	−208.455		0.13
Butyl Butanoate (1) + Ethanol (2)						
$y_1 + x_1$ vs x_1	5.634	−0.879	−4.600	−7.662		0.001
T vs x_1	1.285	−84.869	90.705	−381.257		0.57
T vs y_1	0.159	−24.085	994.353	−1642.518	747.268	0.19

appeared in the butyl ester concentration in the vapor phase, due possibly to a bad recirculation of that phase by pressurization problems and hence inestability in the equilibrium conditions.

Of the binary mixtures considered here, only the system butyl methanoate + ethanol presented a minimum azeotrope. The position of the singularity was found by applying the corresponding correlations and solving the equations $y_1 - x_1 = 0$ and $(\partial T/\partial x_1) = 0$ simultaneously. The position of the azeotrope was at $x_1 = y_1 = 0.088$ and $T = 350.9$ K. The interpolated values in the plot of Figure 4 are similar ($x_1 = 0.080$, $T = 351.0$ K) to the calculated ones.

Prediction of VLE. The ASOG group contribution method (Tochigi et al., 1990) and several versions of the UNIFAC group contribution model (Fredenslund et al., 1975; Larsen et al., 1986; Weidlich and Gmehling, 1987) were used to estimate the VLE values for all the butyl ester (1) + ethanol (2) mixtures. The activity coefficients, γ_i, and vapor phase concentrations, y_1, were contrasted using eq 2 in all cases. Table 8 presents a quantitative assessment of all the theoretical predictions. The version of the UNIFAC model proposed by Weidlich and Gmehling (1987) proved to be best at predicting the activity coefficients, with a mean error of less than 8% for the four systems, comparable to the result achieved using the ASOG model. The version of the UNIFAC model proposed by Larsen et al. (1986) yielded a mean error of 12.5%; that version of the model was not applicable to the set of mixtures containing butyl methanoate, because no values for the OH/HCOO interaction were available. The mean errors for the estimates of the γ_i values produced by the version of Fredenslund et al. (1975) depended on the interaction pair considered and ranged from 11% (for OH/COO) to 27% (for CCOH/COOC). Oddly, the interaction pair that yielded the best VLE value estimates, OH/COO, has been recommended for non-alkyl esters (Macedo et al., 1983). In general, in all cases except for the mixture butyl metha-

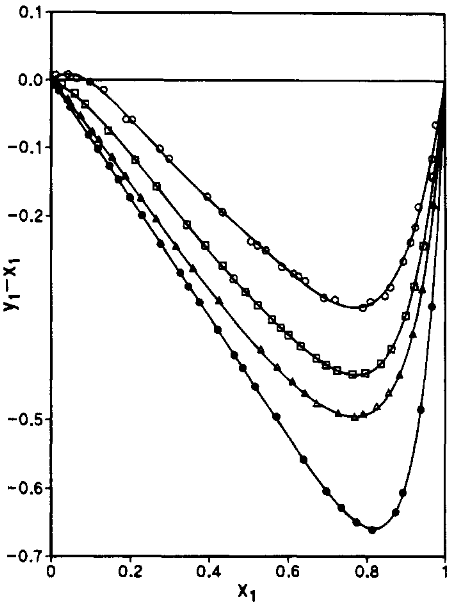

Figure 4. Representation of $y_1 - x_1$ vs x_1 for the mixtures formed by ethanol (2) with (○) butyl methanoate (1), (□) butyl ethanoate (1), (△) butyl propanoate (1), and (●) butyl butanoate (1).

Table 8. Mean Errors $\bar{e}(\gamma_i)$[a] and Mean Deviation $\delta(y_1)$ Obtained in the Prediction of VLE Using Different Group Contribution Models

	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) + Ethanol (2)									
$\bar{e}(\gamma_i)$	6.2	8.6		6.1		4.8		3.4	
$\delta(y_1)$	0.010	0.009		0.005		0.007		0.005	
$\delta_{\max}(y_1)$	0.019	−0.031		−0.014		0.015		−0.014	
(at $x_1 =$)	(0.614)	(0.189)		(0.189)		(0.614)		(0.189)	
Butyl Ethanoate (1) + Ethanol (2)									
$\bar{e}(\gamma_i)$	5.7		11.7	12.3	14.5	7.7	5.2		4.7
$\delta(y_1)$	0.008		0.007	0.009	0.011	0.005	0.005		0.010
$\delta_{\max}(y_1)$	−0.017		−0.018	−0.019	−0.019	−0.018	−0.017		−0.017
(at $x_1 =$)	(0.943)		(0.943)	(0.943)	(0.943)	(0.943)	(0.943)		(0.943)
Butyl Propanoate (1) + Ethanol (2)									
$\bar{e}(\gamma_i)$	11.5		28.2	22.7	36.2	17.6	18.1		13.0
$\delta(y_1)$	0.009		0.008	0.007	0.008	0.007	0.009		0.008
$\delta_{\max}(y_1)$	0.019		−0.017	−0.017	0.018	−0.016	−0.023		−0.022
(at $x_1 =$)	(0.643)		(0.941)	(0.941)	(0.226)	(0.941)	(0.941)		(0.941)
Butyl Butanoate (1) + Ethanol (2)									
$\bar{e}(\gamma_i)$	8.0		22.4	16.1	30.1	12.7	14.3		8.3
$\delta(y_1)$	0.007		0.008	0.007	0.011	0.006	0.006		0.007
$\delta_{\max}(y_1)$	−0.037		−0.037	−0.041	−0.038	−0.037	−0.033		−0.044
(at $x_1 =$)	(0.966)		(0.966)	(0.966)	(0.966)	(0.966)	(0.966)		(0.966)

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

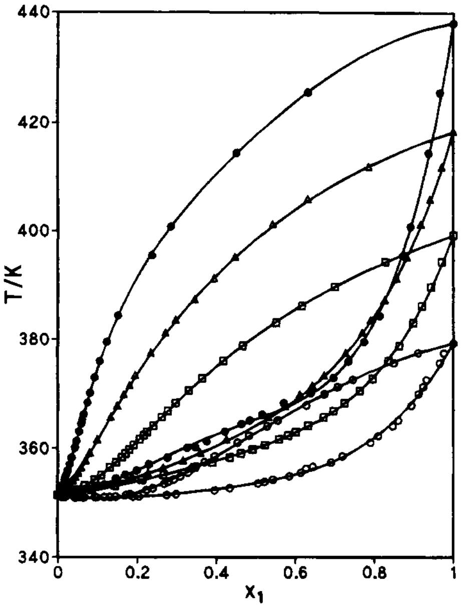

Figure 5. Representation of T vs x_1 or y_1 for the mixtures formed by ethanol (2) with (0) butyl methanoate (1), (□) butyl ethanoate (1), (△) butyl propanoate (1), and (●) and butyl butanoate (1).

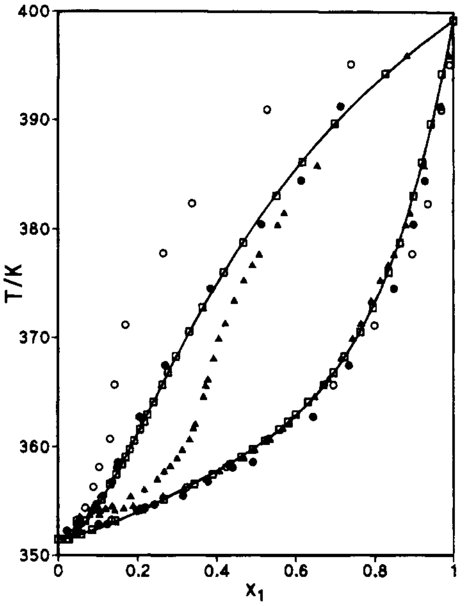

Figure 6. Comparison of our experimental data in T vs x_1 or y_1 for the mixture butyl ethanoate (1) + ethanol (2): (□) experimental data; (0) Beregovykh et al. (1971); (●) Shono and Kanazawa (1969); (▲) Ortega et al. (1987).

noate + ethanol the major differences in the prediction appear for high butyl ester concentrations.

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