

VAPOR-LIQUID EQUILIBRIA FOR MIXTURES OF SEVERAL BUTYL ESTERS (METHANOATE TO BUTANOATE) AND 1-PROPANOL AT 101.32 kPa.

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Isobaric p - T - x - y values for four binary mixtures composed of several butyl esters (from methanoate to butanoate) with *n*-propanol at 101.32 kPa have been measured using a dynamic method. All mixtures presented positive deviations from ideality and they were found to be thermodynamically consistent with the point-to-point test, being then correlated with suitable equations. An azeotrope at $x_1 = 0.300$ and $T = 363.7$ K was found for the mixture (x_1 butyl methanoate+ x_2 *n*-propanol). The group contribution models gave acceptable estimations for the γ_i values.

Introduction

Theoretical validation of vapor-liquid equilibrium (VLE) studies calls for fitting model parameters to a solid experimental database. For that reason, the present paper presents isobaric VLE values for binary mixtures consisting of butyl esters (from methanoate to butanoate) and *n*-propanol at 101.32 kPa, another contribution by our laboratory in the series of studies under way on VLE values for (alkylester+alcohol) systems (Ortega *et al.*, 1990; Ortega and Galván, 1994; González and Ortega, 1995).

The only literature values found were for the mixture (butylethanoate+*n*-propanol) published by [Beregovykh, V.V., V.S. Timofeev and R.N. Lukyanova; Uch. Zap. Mosk. Inst. *Tonkoi Khim.*, 1, 38, 1971 (see Gmehling *et al.*, 1988)] and by Ortega *et al.* (1987) and a report by Horsley (1952) of an azeotrope for the mixture (butyl methanoate+*n*-propanol). Our experimental determinations were compared with the theoretical predictions produced by the ASOG (Kojima and Tochigi, 1979) and UNIFAC (Fredenslund *et al.*, 1975) group-contribution models, including the modified versions of the UNIFAC model proposed by Larsen *et al.* (1986) and Weidlich and Gmehling (1987).

1. Experimental Section

1.1 Chemicals

The chemical components employed in the various experiments were purchased from among the highest available commercial grades: butyl methanoate and butyl propanoate, Aldrich +99 mole%; *n*-propanol, butyl ethanoate, and butyl butanoate, Fluka >99 mole%. The

components were not subjected to special treatment, but prior to use they were degassed using ultrasound for several hours and then dried on a molecular sieve (Fluka, type 0.3 nm). The physical properties of the butyl esters were not significantly different from recently published values (González and Ortega, 1995). For the *n*-propanol, the values were: ρ (298.15 K) = 799.60 kg·m⁻³, 799.60 (Riddick *et al.*, 1986), 799.75 (TRC, 1993); n_D (298.15 K) = 1.3835, 1.38370 (Riddick *et al.*, 1986), 1.38370 (TRC, 1993); and $T_{b,2}$ = 370.35 K, 370.30 (Riddick *et al.*, 1986), 370.35 (TRC, 1993).

1.2 Equipment and procedure

The equipment employed in the present study was an equilibrium still in which the two phases were refluxed. Load capacity was approximately 60 cm³. A more detailed description has already been published elsewhere (Ortega *et al.*, 1986; Ortega and Susial, 1991).

Samples of the liquid and vapor phases were analysed densimetrically, using an Anton Paar model DMA-55 vibrating tube densimeter calibrated with water and *n*-nonane (Ortega *et al.*, 1985a). The precision of the density readings was ± 0.02 kg·m⁻³. The composition of each phase was calculated to a precision of ± 0.001 units for the liquid phase, somewhat more for the vapor phase, employing the correlations of excess molar volume, V^E , on ester concentration, x_1 , using the density, ρ , values. The composition values thus calculated did not differ significantly from those calculated using more direct polynomial expressions of ρ on x_1 .

2. Experimental Results

2.1 Densities

For each of the binary systems composed of a butyl

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Table 1 Densities and excess volumes for butyl esters (1)+*n*-propanol (2) at 298.15 K

x_1	ρ [kg m ⁻³]	$10^3 v^E$ [m ³ mol ⁻¹]	x_1	ρ [kg m ⁻³]	$10^3 v^E$ [m ³ mol ⁻¹]
Butyl Methanoate (1) + <i>n</i> -Propanol (2)					
0.0297	803.25	12	0.4950	850.72	143
0.0774	809.06	36	0.5769	857.37	148
0.1137	813.26	57	0.6125	860.15	146
0.2030	823.14	90	0.7368	869.41	125
0.3040	833.50	110	0.7838	872.74	110
0.3788	840.55	128	0.9005	880.61	63
0.4120	843.55	133	0.9543	884.02	42
Butyl Ethanoate (1) + <i>n</i> -Propanol (2)					
0.0430	804.94	26	0.4589	843.96	166
0.0871	810.07	52	0.5151	847.98	170
0.1409	815.95	79	0.5768	852.16	170
0.1915	821.09	105	0.6344	855.86	164
0.2507	826.78	124	0.7315	861.67	149
0.3139	832.45	138	0.7963	865.35	125
0.3603	836.34	148	0.8872	870.16	89
0.4011	839.59	156			
Butyl Propanoate (1) + <i>n</i> -Propanol (2)					
0.0495	806.42	23	0.4871	845.49	137
0.0931	811.66	39	0.5361	848.54	142
0.1485	817.75	60	0.5782	851.05	141
0.1928	822.20	77	0.6344	854.23	136
0.2327	825.97	89	0.7159	858.48	127
0.3263	834.00	109	0.7802	861.56	120
0.3860	838.54	124	0.8849	866.32	78
0.4324	841.84	131	0.9307	868.37	38
Butyl Butanoate (1) + <i>n</i> -Propanol (2)					
0.0500	806.45	28	0.4611	841.30	147
0.1022	812.60	44	0.5151	844.33	155
0.1607	818.61	73	0.5861	848.04	154
0.2159	823.73	91	0.7284	854.51	142
0.2535	826.94	100	0.8113	857.82	124
0.3107	831.39	117	0.8484	859.25	107
0.3543	834.50	129	0.8864	860.69	82
0.4022	837.69	138	0.9349	862.41	55

Table 2 Coefficients A_i and k in Eq. 1 and standard deviations, s (v^E)

Mixture	k	A_0	A_1	A_2	$10^3 s$ (v^E) [m ³ mol ⁻¹]
Butyl Methanoate (1) + <i>n</i> -Propanol (2)	5.89	515	396	—	3
Butyl Ethanoate (1) + <i>n</i> -Propanol (2)	1.50	675	-224	535	2
Butyl Propanoate (1) + <i>n</i> -Propanol (2)	0.80	492	-120	409	3
Butyl Butanoate (1) + <i>n</i> -Propanol (2)	1.18	520	-18	458	2

ester (1) +*n*-propanol (2) considered, pairs of values for ρ (298.15±0.01) K and x_1 were determined and compared, and the uniform distribution of v^E values revealed the volumetric behavior of the mixtures. The data are listed in Table 1, and the precision of the mole fraction was better than ±10⁻⁴ and the precision of the v^E values ±2·10⁻⁹ m³·mol⁻¹. The excess molar volumes were correlated using an expression of the type:

$$10^3 \cdot v^E / [\text{m}^3 \cdot \text{mol}^{-1}] = x_1 x_2 \sum A_i \{x_1 / [x_1 + k(1 - x_1)]\}^i \quad (1)$$

Table 2 presents the values of the coefficients A_i and k and the corresponding standard deviations, s (v^E). The only literature values for v^E found were the values for the

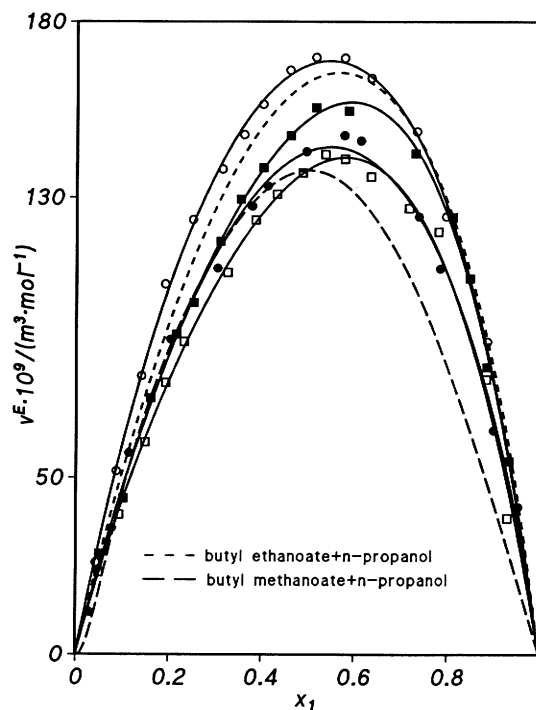


Fig. 1 Excess molar values at 298.15 K for the mixtures (x_1 butyl esters+ x_2 *n*-propanol). Experimental and literature values: (●), butyl methanoate; (○), butyl ethanoate; (□), butyl propanoate; (■), butyl butanoate; —, Ortega (1985); ---, Ortega et al. (1985b)

mixtures (butyl methanoate and butyl ethanoate+*n*-propanol) reported by our laboratory previously (Ortega, 1985; Ortega et al., 1985b). Figure 1 graphically compares the present results and the literature values. At high ester concentrations, the mixing volumes observed for the system (butyl methanoate+*n*-propanol) were somewhat higher than the literature (Ortega, 1985), presenting an estimated error of around 15%. The differences with respect to the literature (Ortega et al., 1985b) for the mixture (butyl ethanoate+*n*-propanol) were less than 6%.

2.2 Vapor-liquid equilibria. Results and discussion

The T - x - y values for the isobaric vapor-liquid equilibria for the mixtures considered in this study at (101.32±0.02) kPa appear in the first three columns in Table 3. The fourth and fifth columns in that Table set out the values of the activity coefficients for the liquid phase, calculated using the equation:

$$\phi_i P y_i = \gamma_i P_i^o x_i \phi_i^o \exp [v_i^L (p - P_i^o) / RT] \quad (2)$$

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

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

The second virial coefficients for the pure components and mixtures thereof were calculated according to the method put forward by Tsonopoulos (1974). Variations in the molar volumes, v_i^L , with temperature were calculated using a modified version of Rackett's equation, see

Table 3 Vapor-Liquid Equilibrium Data for Butyl Alkanoates+n-Propanol at 101.32 kPa

T/K	x_1	y_1	γ_1	γ_2
Butyl Methanoate (1) +n-Propanol (2)				
369.70	0.0065	0.0157	3.248	0.998
369.37	0.0236	0.0437	2.526	0.998
369.00	0.0493	0.0818	2.286	0.998
368.71	0.0691	0.1118	2.249	0.997
368.37	0.1086	0.1581	2.044	0.999
368.12	0.1463	0.1993	1.928	1.001
367.94	0.1790	0.2289	1.819	1.009
367.86	0.2058	0.2507	1.739	1.017
367.78	0.2407	0.2749	1.634	1.032
367.73	0.2962	0.2982	1.442	1.080
367.74	0.3375	0.3200	1.358	1.111
367.77	0.3834	0.3442	1.284	1.150
367.82	0.4263	0.3633	1.217	1.198
367.91	0.4654	0.3804	1.164	1.247
367.98	0.4816	0.3953	1.166	1.252
368.03	0.4907	0.4000	1.156	1.262
368.05	0.4920	0.4009	1.155	1.263
368.06	0.5173	0.4012	1.099	1.327
368.18	0.5283	0.4101	1.096	1.333
368.22	0.5513	0.4205	1.075	1.374
368.36	0.5727	0.4338	1.063	1.403
368.55	0.6093	0.4534	1.038	1.470
368.76	0.6270	0.4711	1.041	1.479
369.30	0.6666	0.5016	1.025	1.529
369.85	0.6992	0.5322	1.019	1.559
370.58	0.7376	0.5712	1.013	1.595
371.42	0.7729	0.6156	1.014	1.604
372.11	0.7985	0.6504	1.015	1.604
372.84	0.8232	0.6854	1.014	1.603
373.56	0.8478	0.7201	1.012	1.615
374.34	0.8732	0.7590	1.011	1.624
375.46	0.8977	0.7981	0.999	1.622
376.35	0.9176	0.8359	0.996	1.587
377.31	0.9425	0.8843	0.997	1.550
378.15	0.9664	0.9298	0.997	1.562
Butyl Ethanoate (1) +n-Propanol (2)				
370.40	0.0320	0.0187	1.375	0.996
370.47	0.0480	0.0280	1.373	1.000
370.51	0.0857	0.0498	1.366	1.016
370.59	0.1193	0.0698	1.370	1.030
370.83	0.1483	0.0867	1.358	1.037
371.14	0.1826	0.1069	1.347	1.045
371.57	0.2182	0.1285	1.336	1.049
371.92	0.2487	0.1459	1.316	1.057
372.38	0.2771	0.1619	1.291	1.060
372.81	0.3113	0.1799	1.259	1.073
373.29	0.3432	0.1981	1.238	1.081
373.80	0.3718	0.2149	1.220	1.087
374.40	0.4082	0.2334	1.184	1.103
374.63	0.4205	0.2417	1.182	1.105
375.05	0.4437	0.2540	1.161	1.116
375.21	0.4548	0.2583	1.146	1.126
375.78	0.4818	0.2767	1.139	1.132
375.94	0.4900	0.2799	1.127	1.139
376.92	0.5369	0.3072	1.094	1.167
378.03	0.5795	0.3367	1.073	1.184
379.34	0.6242	0.3700	1.051	1.203
381.04	0.6708	0.4128	1.036	1.208
383.15	0.7273	0.4639	1.008	1.242
385.75	0.7867	0.5379	1.000	1.257
388.42	0.8375	0.6114	0.987	1.273
391.07	0.8856	0.6942	0.982	1.309
393.68	0.9272	0.7817	0.980	1.354
396.45	0.9690	0.8921	0.991	1.446

T/K	x_1	y_1	γ_1	γ_2
Butyl Propanoate (1) +n-Propanol(2)				
370.37	0.0306	0.0209	2.878	0.993
370.49	0.0476	0.0237	2.091	1.003
370.92	0.0755	0.0348	1.911	1.006
371.51	0.1131	0.0490	1.756	1.012
372.21	0.1482	0.0613	1.638	1.014
372.93	0.1846	0.0739	1.546	1.019
373.72	0.2300	0.0881	1.440	1.033
374.46	0.2696	0.1007	1.369	1.046
375.41	0.3161	0.1144	1.285	1.064
376.48	0.3673	0.1328	1.239	1.085
377.76	0.4142	0.1516	1.201	1.097
379.20	0.4675	0.1731	1.159	1.119
380.62	0.5232	0.1921	1.097	1.164
380.89	0.5261	0.1980	1.115	1.152
381.69	0.5674	0.2081	1.059	1.213
382.75	0.5804	0.2206	1.060	1.188
383.18	0.5927	0.2293	1.064	1.193
383.94	0.6078	0.2392	1.056	1.193
384.43	0.6247	0.2466	1.043	1.215
385.47	0.6467	0.2628	1.039	1.220
387.51	0.6828	0.2924	1.027	1.221
388.82	0.7082	0.3131	1.018	1.236
389.85	0.7229	0.3289	1.014	1.231
391.62	0.7503	0.3572	1.005	1.237
393.18	0.7720	0.3827	0.998	1.240
395.48	0.8014	0.4222	0.990	1.241
398.19	0.8313	0.4708	0.982	1.233
400.69	0.8581	0.5191	0.975	1.238
403.72	0.8872	0.5814	0.968	1.241
407.17	0.9151	0.6586	0.965	1.220
411.82	0.9467	0.7803	0.973	1.100
Butyl Butanoate (1) +n-Propanol (2)				
370.84	0.0340	0.0125	2.921	0.988
371.87	0.1018	0.0280	2.098	1.008
373.04	0.1713	0.0370	1.580	1.038
373.37	0.1895	0.0394	1.501	1.046
374.66	0.2559	0.0482	1.294	1.079
375.19	0.2810	0.0517	1.241	1.092
375.57	0.2973	0.0540	1.208	1.100
377.13	0.3629	0.0643	1.114	1.136
377.88	0.3925	0.0689	1.074	1.156
378.63	0.4205	0.0738	1.044	1.175
379.58	0.4495	0.0804	1.029	1.188
380.94	0.4909	0.0900	1.005	1.214
381.30	0.5034	0.0919	0.988	1.227
382.56	0.5350	0.1010	0.977	1.244
384.20	0.5794	0.1123	0.948	1.286
386.18	0.6203	0.1292	0.951	1.310
387.89	0.6526	0.1422	0.939	1.335
391.66	0.7150	0.1764	0.937	1.386
394.52	0.7520	0.2040	0.938	1.409
398.42	0.7919	0.2467	0.950	1.412
409.01	0.8694	0.3717	0.942	1.383
411.01	0.8842	0.4022	0.945	1.405
416.33	0.9155	0.4908	0.955	1.423
419.60	0.9320	0.5510	0.961	1.432
423.03	0.9470	0.6199	0.968	1.427
424.61	0.9533	0.6537	0.972	1.418
428.22	0.9666	0.7361	0.981	1.382

Spencer and Danner (1972). The values of the Antoine constants, A , B , C , in the correlations for the vapor pressure, p_i° values on temperature, T , for the butyl esters and the n -propanol were taken from previous papers by González and Ortega (1995) and Ortega *et al.* (1990).

In view of the few vapor pressure values for butyl esters reported in the literature and the appreciable influ-

ence of those values on calculations of the activity coefficients, the values of γ_i calculated using the Antoine correlations obtained at our laboratory (González and Ortega, 1995) were contrasted with the literature values. The mean error in the calculation of all the γ_i values for (butyl methanoate + n -propanol) was less than 2% with respect to the constants reported by Boublick *et al.* (1973) and 1% with respect to those published by Riddick *et al.* (1986). The findings for the mixture (butyl ethanoate + n -propanol) were similar. Using the constant values published by Gmehling *et al.* (1990) instead of the constants estimated in our laboratory, the difference in the values calculated for

Table 4 Parameters Obtained for Eq. 4 and Standard Deviations, $s(Q_k)$, for the Differents Correlations

Correlation	k	A_0	A_1	A_2	A_3	$s(Q_k)$
Butyl Methanoate (1) +n-Propanol (2)						
Q_1 vs. x_1	0.620	0.887	-2.110	—	—	0.004
Q_2 vs. x_1	1.12	-40.91	120.29	-272.65	167.49	0.12
Q_3 vs. y_1	0.26	-52.31	160.50	-310.63	196.46	0.06
Q_4 vs. x_1	7.128	0.804	-0.508	0.698	-1.068	0.002
Butyl Ethanoate (1) +n-Propanol (2)						
Q_1 vs. x_1	3.713	-0.371	-2.266	—	—	0.002
Q_2 vs. x_1	0.77	-31.18	15.44	-37.59	—	0.10
Q_3 vs. y_1	0.63	-30.39	34.47	55.85	-57.62	0.05
Q_4 vs. x_1	1.220	0.558	0.233	-0.816	—	0.004
Butyl Propanoate (1) +n-Propanol (2)						
Q_1 vs. x_1	4.193	-0.546	-3.740	—	—	0.004
Q_2 vs. x_1	0.54	-49.79	57.10	-106.99	—	0.21
Q_3 vs. y_1	0.20	-52.24	148.11	-71.40	—	0.08
Q_4 vs. x_1	1.925	0.807	-1.776	3.719	-3.538	0.002
Butyl Butanoate (1) +n-Propanol (2)						
Q_1 vs. x_1	8.994	-0.774	-8.569	—	—	0.003
Q_2 vs. x_1	2.51	-54.21	-104.39	-103.21	—	0.18
Q_3 vs. y_1	0.09	-108.54	491.15	-346.62	—	0.16
Q_4 vs. x_1	1.856	1.048	-3.337	5.461	-3.740	0.003

the γ_i coefficients for the system (butyl butanoate + n -propanol) was 4%. No comparisons were possible for the system containing butyl propanoate, because the constant values given by Boublick *et al.* (1973) were calculated for a very different temperature range from the range employed for that system in the present study.

The data for the mixtures considered were found to be consistent according to the point-to-point test of Van Ness *et al.* (1973) as proposed by Fredenslund *et al.* (1977b), though, as already stated above, certain modifications were made in the calculations of the values for the virial coefficients, B_{ii} , and the molar volumes, v_i^L . The composition and temperature data and the data for the adimensional function of the Gibbs free energy, g^E/RT , were fit using the polynomial function, similar to Eq. (1):

$$Q_k = x_1 x_2 \sum A_i \{x_1 / [x_1 + k(1 - x_1)]\}^i \quad (4)$$

where Q_k is the function to be fit and x_1 is the composition of the liquid phase of the ester. **Table 4** presents the parameter values for Eq. (4) together with the standard deviations, $s(Q_k)$, calculated by correlating the functions $Q_1 = (y_1 - x_1)$, $Q_2 = T - \sum x_i T_{b,i}$, $Q_3 = T - \sum y_i T_{b,i}$ and $Q_4 = g^E/RT$ on x_1 . Function Q_2 and Q_3 were similar to those proposed by Wisniak and Tamir (1976) to correlate temperature versus mole fraction.

Figure 2 (a) plots the experimental values for $(y_1 - x_1)$ on x_1 together with the fitted curves for the different systems considered. **Figure 2** (b) graphically compares the experimental data and the literature values for the mixture butyl ethanoate (1) + n -propanol (2). The composition values displayed large discrepancies with respect to the values published by Beregovykh *et al.* (1971), see Gemhling *et al.* (1988), but the differences with the values reported by Ortega *et al.* (1987) were somewhat smaller. **Figures 3** (a, b) present the temperature plots. The

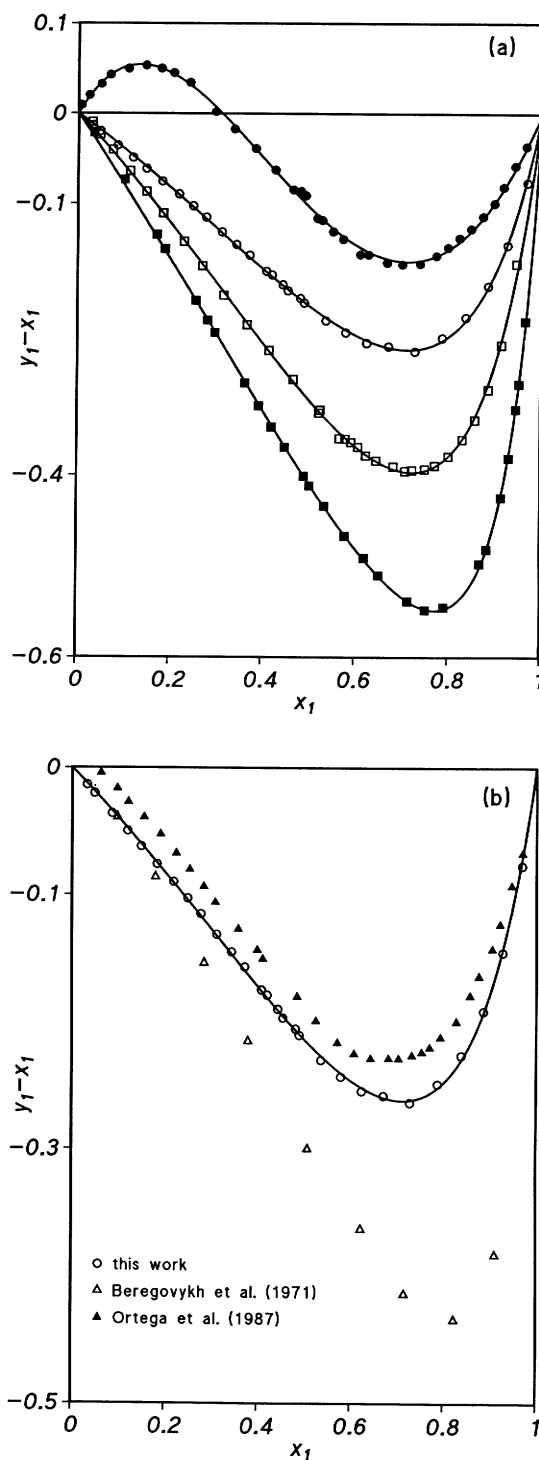


Fig. 2 Plot of $(y_1 - x_1)$ vs x_1 of the mixtures x_1 butyl esters + $x_2 n$ -propanol (a), and the comparison between our results and those from the literature, (b), for x_1 butyl ethanoate + $x_2 n$ -propanol at 101.32 kPa. (●), methanoate; (○), ethanoate; (□), propanoate; (■), butanoate; (△), Beregovykh *et al.*, 1971 (see Gemhling *et al.*, 1988); (▲), Ortega *et al.* (1987)

comparison with the literature values showed that the values reported by Beregovykh *et al.* (1971), see Gemhling *et al.* (1988), closely matched our curve for the liquid phase, but there were marked discrepancies for the vapor phase, perhaps ascribable to difficulties affecting operation of the

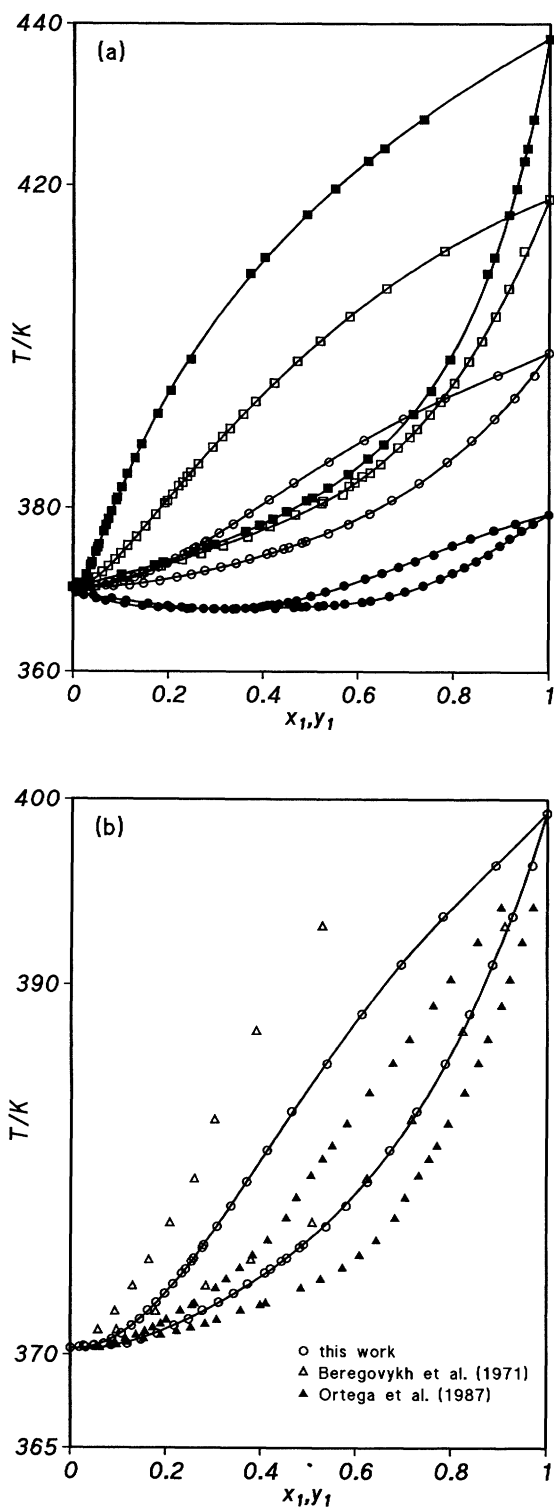


Fig. 3 Representation of T vs x_1, y_1 of the mixtures x_1 butyl esters + x_2 n -propanol (a), and the comparison between our results and those from the literature, (b), for x_1 butyl ethanoate + x_2 n -propanol at 101.32 kPa. (●), methanoate; (○), ethanoate; (□), propanoate; (■), butanoate; (△), Beregovykh *et al.*, 1971 (see Gmehling *et al.*, 1988); (▲), Ortega *et al.* (1987)

reflux mechanism. This same consideration with respect to the recirculation of the phases was also applicable to the values reported earlier (Ortega *et al.*, 1987). The thermo-

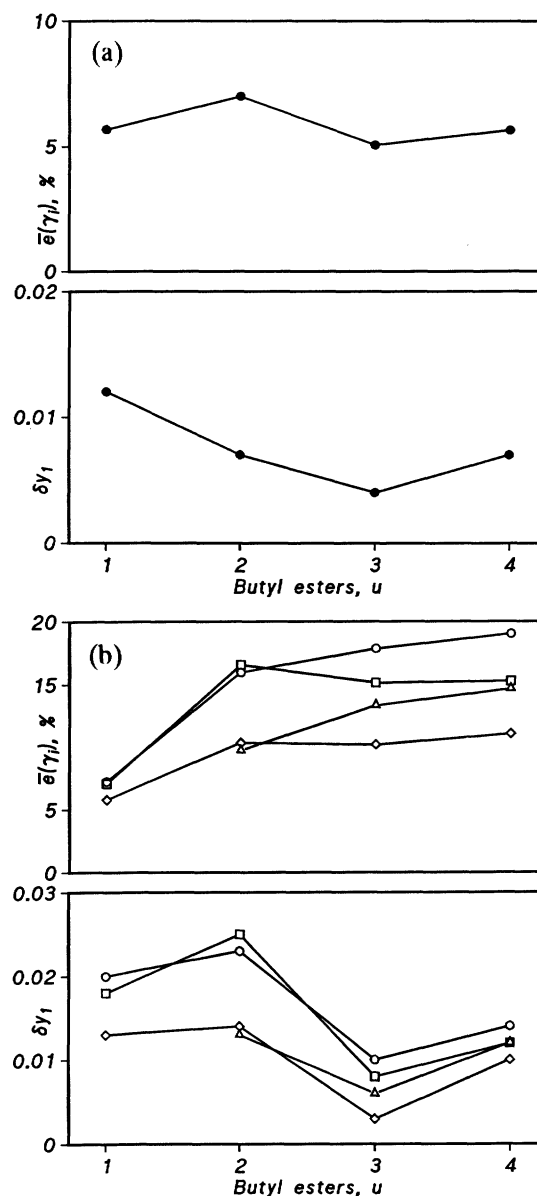
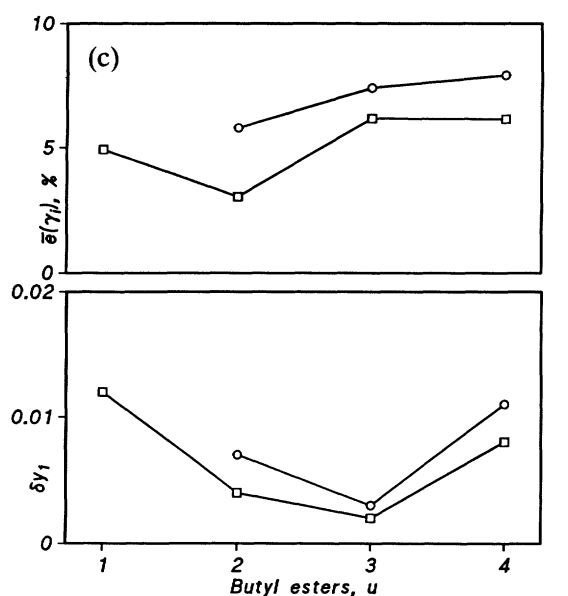


Fig. 4 Mean deviation δy_1 , and average error, $\bar{e}(\gamma_i)$, obtained in the prediction of the mixtures $C_{u-1}H_{2u-1}CO_2C_4H_9$ ($u = 1$ to 4) + $C_3H_5CH_2(OH)$ for the following cases. (a): ASOG (Tochigi *et al.*, 1990); (b): UNIFAC, (○), $OH/HCOO$ (Hansen *et al.*, 1991), $OH/COOC$ (Gmehling *et al.*, 1982), (□), COH/COO (Fredenslund *et al.*, 1975), (△), $CCOH/COOC$ (Fredenslund *et al.*, 1977a), (◇), OH/COO (Macedo *et al.*, 1983); (c): Modified UNIFAC, (○), $OH/COOC$ (Larsen *et al.*, 1987), (□), $OH/HCOO$ (Gmehling *et al.*, 1993)

dynamic consistency of the literature values was negative in both cases.

The mixture (butyl methanoate + n -propanol) was the only one of the systems considered in this study that had a minimum azeotrope. The correlations for the functions Q_1, Q_2 , and Q_3 , whose coefficients appear in Table 4, were employed to solve the system of equations: $(y_1 - x_1) = 0$ and $(\partial T / \partial x_1) = (\partial T / \partial y_1) = 0$ for the coordinates for the azeotrope at $x_1 = y_1 = 0.300, T = 367.73$ K. The coordinates of this same singularity were estimated at $T = 368.65$ K,



$$\delta(\gamma_i) = \sum |y_{i,exp} - y_{i,cal}| / N; \quad \bar{e}(\gamma_i) = \sum (|y_{i,exp} - y_{i,cal}| / y_{i,exp})^{100} / N$$

Fig. 4 Mean deviation $\delta\gamma_i$, and average error, $\bar{e}(\gamma_i)$, obtained in the prediction of the mixtures $C_{u-1}H_{2u-1}CO_2C_4H_9$ ($u = 1$ to 4) + $C_2H_5CH_2(OH)$ for the following cases. (a): ASOG (Tochigi *et al.*, 1990); (b): UNIFAC, (\circ), $OH/HCOO$ (Hansen *et al.*, 1991), $OH/COOC$ (Gmehling *et al.*, 1982), (\square), COH/COO (Fredenslund *et al.*, 1975), (\triangle), $CCOH/COOC$ (Fredenslund *et al.*, 1977a), (\diamond), OH/COO (Macedo *et al.*, 1983); (c): Modified UNIFAC, (\circ), $OH/COOC$ (Larsen *et al.*, 1987), (\square), $OH/HCOO$ (Gmehling *et al.*, 1993)

$x_1 = y_1 = 0.249$ in the literature (Horsley, 1952).

3. Prediction of VLE using Different Group-Contribution Models

To check the accuracy of the predictions of vapor-liquid equilibria for all the butyl ester (1) + n -propanol (2) systems, the activity coefficient, γ_i , and vapor phase composition, y_i , values from Table 3 were compared with the estimates produced by the different group-contribution models, namely, the ASOG (Kojima and Tochigi, 1979) model and the different versions of the UNIFAC model, Fredenslund *et al.* (1975), Larsen *et al.* (1986) and Weidlich and Gmehling (1987). **Figures 4 (a-c)** present a qualitative valuation for the theoretical estimates obtained using the different models. The ASOG model and the version of the UNIFAC model proposed by Weidlich and Gmehling (1987) yielded the best predictions of the activity coefficients, with a mean overall error of less than 6% for the γ_i values for the four systems considered. The version of the UNIFAC model proposed by Larsen *et al.* (1986) could not be applied for the mixture butyl methanoate (1) + n -propanol (2) because no values for the interaction pair $OH/HCOO$ were available; for the other three mixtures, the mean error of the estimates for the γ_i values achieved using that version of the UNIFAC model was 7%. Finally, the mean error for the predictions of the γ_i values calculated

using the version of the UNIFAC model proposed by Fredenslund *et al.* (1975) depended upon the interaction parameters employed and ranged from 9% for OH/COO to 15% for $OH/COOC$. The best results were achieved using the interaction parameter values for OH/COO published by Macedo *et al.* (1983), even though those values were recommended for mixtures containing non-alkyl esters.

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Nomenclature

A, B, C	= Antoine constants	[-]
A_i	= coefficients in Eq. (1)	[-]
B_{ij}	= cross-virial coefficients	[$m^3 \text{ kmol}^{-1}$]
k	= parameter in Eq. (1)	[-]
N	= number of experimental points	[-]
p	= total pressure	[kPa]
p_i^o	= vapor pressure of pure component i	[kPa]
R	= universal gas constant	[$\text{JK}^{-1} \text{ kmol}^{-1}$]
s	= standard deviation	[-]
T	= temperature	[K]
T_b	= boiling temperature of pure component i	[K]
v_i^L	= molar volume of pure component i	[$m^3 \text{ kmol}^{-1}$]
x	= liquid-phase molar fraction	[-]
y	= vapor-phase molar fraction	[-]
ρ	= density	[kg m^{-3}]
γ_i	= activity coefficient of component i	[-]
ϕ_i	= fugacity coefficient of component i	[-]
δ	= difference between two values	[-]

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