VAPOR-LIQUID EQUILIBRIA AT 101.32 kPa MIXTURES OF BUTYL ESTERS AND PROPAN-2-OL

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The concentrations of the vapor-liquid equilibria have been measured in a small capacity recirculating still for the binaries composed of four butyl esters (from methanoate to butanoate) and propan-2-ol at a constant pressure of 101.32 kPa. VLE data were thermodynamically verified with the point-to-point test and the predictions made using several group-contribution models were acceptable but with some exceptions. An azeotrope was found for (x_1 butyl methanoate+ x_2 propan-2-ol) at $x_1 = y_1 = 0.038$ and $T = 354.9$ K.

Introduction

Continuing a series of studies on the isobaric vapor-liquid equilibria (VLEs) of mixtures of butyl esters+n-alkanols carried out by our laboratory, the present paper reports VLE values at 101.32 kPa for the first four butyl esters (from methanoate to butanoate) and propan-2-ol. A search of the literature did not yield any references to the existence of azeotropes for these mixtures but did disclose experimental isobaric VLE values for the mixture consisting of (butyl ethanoate+propan-2-ol), see Gmehling *et al.* (1982). In addition, several group-contribution models were used to estimate the VLE values to evaluate the suitability of such models for mixtures containing isomeric alkanols.

1. Experimental Section

1.1 Chemicals

The components employed were of the highest available commercial grade. The butyl methanoate and propanoate were + 99% from Aldrich, while the propan-2-ol and butyl ethanoate and butanoate were > 99% from Fluka. All components were degassed using ultrasound for several hours and then dried on a molecular sieve (Fluka, 0.3 nm) before use. The physical properties of the butyl esters were determined experimentally and matched the values reported recently by González and Ortega (1995). The following values were recorded for the propan-2-ol: ρ (298.15 K) = 780.85 kgm⁻³, 781.26 (Riddick *et al.*, 1986); 780.82 (TRC, 1993); n (D , 298.15 K) = 1.3752, 1.3752 (Riddick *et al.*, 1986); 1.37527 (TRC, 1993); and $T_{b,2}^o$ = 355.40 K, 355.39 (Riddick *et al.*, 1986); 355.48 (TRC, 1993).

1.2 Equipment and Procedure

An ebulliometer of the type in which both phases are refluxed was employed to achieve the equilibrium vapor

and liquid phases. This equipment was described earlier by Ortega and Susial (1991b). Samples of both phases were analyzed using an Anton Paar model DMA-55 densimeter previously calibrated with water and n-nonane (see Ortega *et al.*, 1985). The density on concentration curves for the (x_1 butyl ester+ x_2 propan-2-ol) mixtures were obtained using a simple polynomial expression, namely, $\rho = \sum A_i x_i^i$ after verifying the uniform distribution of v^E on x_1 . By regressing that equation the equilibrium vapor, y_1 , and liquid, x_1 , phase compositions were then calculated to a precision less than ± 0.002 for the two phases.

2. Experimental Results

2.1 Densities and Excess Volumes

For each of the binary (x_1 butyl ester+ x_2 propan-2-ol) systems considered, the density, ρ , was determined to an accuracy of ± 0.02 kgm⁻³ and the concentration, x_1 , was determined to a precision of $\pm 2 \cdot 10^{-4}$, at $T = (298.15 \pm 0.01)$ K. These values were then used to calculate the v^E values, which were correlated with the concentration of the corresponding ester using the equation:

$$10^3 v^E / (m^3 mol^{-1}) = x_1 x_2 \sum V_i \{x_1 / [x_1 + kx_2]\}^i \quad (1)$$

Table 1 presents the x_1 , ρ , and v^E values for each of the binary mixtures considered in this study, while **Table 2** presents the values of the coefficients V_i calculated using a least-squares procedure for a k values yielding the minimum standard deviation, s (v^E), in Eq. (1). **Fig. 1** plots these experimental values and the corresponding fits. No v^E values for these four (butyl ester+propan-2-ol) mixtures were found in the literature. All the v^E values were positive, giving rise to volumetric expansion effects, which together with the behavior of other thermodynamic properties has recently been under investigation by our laboratory to explain variations in such magnitudes with chain length and the nature of the components employed.

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Table 1 Densities and Excess Volumes for (x_1 Butyl Alkanoates+Propan-2-ol) at 298.15 K

x_1	ρ [kgm ⁻³]	$10^9 v^E$ [m ³ mol ⁻¹]	x_1	ρ [kgm ⁻³]	$10^9 v^E$ [m ³ mol ⁻¹]
Butyl Methanoate+Propan-2-ol					
0.0490	787.99	51	0.5306	845.56	320
0.1072	796.22	96	0.6134	853.88	300
0.1583	802.79	166	0.6428	856.98	261
0.2627	815.90	241	0.7054	862.97	225
0.3331	824.13	286	0.7687	868.81	183
0.3759	828.98	304	0.8296	874.19	143
0.4266	834.58	316	0.8963	879.83	98
0.4750	839.77	322	0.9752	886.31	30
Butyl Ethanoate+Propan-2-ol					
0.0628	789.88	93	0.5240	840.00	371
0.1131	796.62	148	0.5769	844.63	351
0.1628	802.68	221	0.6426	849.97	336
0.1996	807.18	245	0.6979	854.40	297
0.2579	813.75	300	0.7738	860.00	260
0.2983	818.18	321	0.8113	862.68	234
0.4020	828.74	362	0.8803	867.53	164
0.4682	835.00	371	0.9622	873.06	60
Butyl Propanoate+Propan-2-ol					
0.0564	789.72	50	0.5453	841.42	325
0.0851	793.78	87	0.6109	846.35	319
0.1623	803.97	162	0.6761	851.02	292
0.2186	810.69	209	0.7472	855.67	271
0.2561	814.98	224	0.7952	858.77	233
0.3474	824.32	278	0.8305	861.03	191
0.3836	827.70	300	0.9550	868.32	56
0.4394	832.73	314			
Butyl Butanoate+Propan-2-ol					
0.0627	790.93	57	0.5878	842.05	330
0.1064	797.07	107	0.6564	846.49	303
0.2004	808.77	187	0.7353	851.24	253
0.2547	814.58	239	0.8031	854.87	227
0.3087	820.06	259	0.8641	858.15	156
0.3865	826.91	315	0.9640	863.04	44
0.5156	837.06	335			

Table 2 Coefficients V_i and k in Eq. (1) and Standard Deviations, s (v^E)

Mixture	k [-]	V_0 [-]	V_1 [-]	V_2 [-]	V_3 [-]	$10^9 s$ (v^E) [m ³ mol ⁻¹]
Butyl Methanoate (1) +Propan-2-ol	0.59	828	1893	-1890	-	8
Butyl Ethanoate (1) +Propan-2-ol	1.04	1475	985	-3281	2603	5
Butyl Propanoate (1) +Propan-2-ol	0.65	1072	378	-	-	5
Butyl Butanoate (1) +Propan-2-ol	0.57	906	1117	-692	-	7

Fig. 2 plots the v^E ($x_1 = 0.5$) values on butyl ester chain length for different normal and isomeric alkanols, including butan-2-ol and methanol (unpublished data); the figure clearly shows the good agreement for the values presented and the similar behavior of the various mixtures. There is no regular increase in the v^E s with the length of the chain R_1 of the butyl alkanate, $R_1\text{COOC}_4\text{H}_9$, because the flexibility of the ester molecules became more conducive to interstitial accommodation of the alkanol joined to the polarity effects for the two types of molecules.

2.2 Vapor-liquid Equilibrium Values

Table 3 lists the isobaric VLE values for T , x_1 , and y_1 at (101.32 ± 0.02) kPa for the (x_1 butyl ester+ x_2 propan-

Fig. 1 Excess molar volmues at 298.15 K for the binaries (x_1 butyl esters+ x_2 propan-2-ol) Experimental and curves: (○), butyl methanoate; (□), butyl ethanoate; (▲), butyl propanoate; (◇), butyl butanoate

Fig. 2 Variation of equimolar excess volmues of the mixtures (butyl esters+alkanols) at 298.15 K as a function of chain-length, u , of butyl alkanate, $C_{u-1}H_{2u-1}COOC_4H_9$ and of alkanols: (▽), methanol (○), ethanol (□), propan-1-ol; (△), butan-1-ol; (★), propan-2-ol; (◇), butan-2-ol

Table 3 Vapor-Liquid Equilibrium Data for (x_1 Butyl Alkanoates + x_2 Propan-2-ol) at 101.32 kPa

T/K	x_1	y_1	γ_1	γ_2
Butyl Methanoate+Propan-2-ol				
355.40	0.0000	0.0000	-	1.000
354.86	0.0292	0.0304	2.286	1.008
354.94	0.0740	0.0676	2.002	1.013
355.10	0.1200	0.1005	1.825	1.022
355.38	0.1666	0.1298	1.681	1.033
355.60	0.2088	0.1622	1.663	1.039
355.93	0.2547	0.1816	1.510	1.064
356.44	0.3208	0.2215	1.436	1.089
356.83	0.3620	0.2411	1.367	1.114
357.29	0.4093	0.2697	1.332	1.138
358.02	0.4681	0.3016	1.270	1.176
358.71	0.5152	0.3270	1.222	1.212
359.50	0.5592	0.3509	1.176	1.248
360.26	0.6038	0.3739	1.132	1.302
361.36	0.6469	0.4029	1.097	1.338
362.45	0.6869	0.4341	1.074	1.375
363.29	0.7122	0.4585	1.064	1.389
363.74	0.7263	0.4704	1.055	1.406
364.66	0.7523	0.4915	1.032	1.443
366.02	0.7913	0.5400	1.032	1.476
367.51	0.8251	0.5755	1.005	1.542
368.37	0.8437	0.6024	1.001	1.569
369.53	0.8665	0.6412	1.000	1.592
371.72	0.9018	0.7072	0.989	1.640
374.28	0.9397	0.7953	0.986	1.713
377.46	0.9820	0.9293	1.001	1.788
379.30	1.0000	1.00000	1.000	-
Butyl Ethanoate+Propan-2-ol				
355.40	0.0000	0.0000	-	1.000
355.41	0.0390	0.1070	1.711	1.011
356.15	0.0866	0.0345	1.519	1.016
356.82	0.1329	0.0530	1.484	1.023
357.32	0.1828	0.0710	1.419	1.045
358.13	0.2296	0.0905	1.400	1.053
359.10	0.2781	0.1079	1.332	1.063
360.32	0.3525	0.1303	1.217	1.104
361.31	0.4032	0.1494	1.179	1.130
362.54	0.4570	0.1696	1.133	1.159
364.30	0.5272	0.1984	1.082	1.207
365.81	0.5781	0.2231	1.055	1.242
367.50	0.6258	0.2544	1.051	1.266
369.40	0.6720	0.2853	1.031	1.297
371.29	0.7132	0.3218	1.030	1.319
373.45	0.7574	0.3605	1.018	1.352
375.53	0.7898	0.3989	1.008	1.384
377.55	0.8208	0.4412	1.007	1.413
378.75	0.8366	0.4642	1.002	1.429
379.32	0.8455	0.4791	1.005	1.442
380.62	0.8602	0.5054	1.001	1.453
382.93	0.8847	0.5535	0.994	1.478
384.89	0.9013	0.5904	0.982	1.491
387.39	0.9234	0.6512	0.982	1.515
389.35	0.9381	0.6985	0.979	1.528
393.15	0.9655	0.8080	0.988	1.562
399.26	1.0000	1.0000	1.000	-

2-ol) mixtures and the values of the activity coefficients for the liquid phase, γ_i , calculated using the equation:

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

The molar volumes, v_i^L , in Eq. (2) were determined for each temperature using a modified version of Rackett's equation (see Spencer and Danner, 1972). The vapor pressure, p_i^o , values were calculated using the Antoine equation with the constants for the butyl esters as reported in an earlier paper by González and Ortega (1995) and the constants for the propa-2-nol as reported by Ortega and Susial (1991a). The values of the fugacity coefficients, ϕ_i and ϕ_i^o , were

T/K	x_1	y_1	γ_1	γ_2
Butyl Propanoate+Propan-2-ol				
355.40	0.0000	0.0000	-	1.000
355.50	0.0291	0.0090	2.214	1.005
356.42	0.0902	0.0266	2.043	1.017
357.26	0.1315	0.0343	1.755	1.024
358.18	0.1788	0.0420	1.529	1.038
359.10	0.2282	0.0511	1.406	1.058
360.05	0.2761	0.0601	1.321	1.078
361.20	0.3307	0.0706	1.243	1.106
362.53	0.3878	0.0832	1.189	1.136
364.10	0.4420	0.0972	1.153	1.160
365.85	0.5012	0.1133	1.113	1.197
368.04	0.5650	0.1347	1.087	1.241
370.75	0.6218	0.1584	1.057	1.264
374.32	0.6796	0.1893	1.024	1.274
377.07	0.7230	0.2184	1.013	1.298
381.10	0.7725	0.2626	0.998	1.310
384.80	0.8098	0.3058	0.985	1.314
388.70	0.8439	0.3562	0.974	1.319
392.40	0.8715	0.4067	0.962	1.323
395.59	0.8936	0.4583	0.960	1.331
398.35	0.9088	0.5018	0.953	1.321
400.73	0.9215	0.5432	0.949	1.317
402.80	0.9323	0.5820	0.947	1.321
403.08	0.9336	0.5883	0.948	1.316
404.49	0.9405	0.6170	0.948	1.316
406.12	0.9478	0.6491	0.946	1.317
409.16	0.9608	0.7165	0.946	1.309
412.89	0.9760	0.8095	0.951	1.306
418.26	1.0000	1.0000	1.000	-
Butyl Butanoate+Propan-2-ol				
355.40	0.0000	0.0000	-	1.000
355.46	0.0457	0.0062	1.976	1.027
356.17	0.0814	0.0101	1.751	1.035
357.13	0.1193	0.0138	1.568	1.037
357.76	0.1668	0.0177	1.402	1.066
358.99	0.2258	0.0228	1.268	1.090
359.73	0.2706	0.0263	1.187	1.122
360.96	0.3168	0.0316	1.160	1.138
362.81	0.3838	0.0394	1.107	1.171
365.17	0.4547	0.0492	1.065	1.203
369.04	0.5444	0.0644	1.002	1.237
373.34	0.6253	0.0844	0.973	1.271
378.08	0.6959	0.1099	0.957	1.303
384.50	0.7695	0.1512	0.949	1.337
390.69	0.8220	0.1967	0.938	1.359
397.20	0.8651	0.2561	0.938	1.375
398.10	0.8707	0.2658	0.940	1.381
402.26	0.8918	0.3110	0.943	1.380
402.45	0.8926	0.3131	0.943	1.379
405.08	0.9051	0.3453	0.946	1.386
406.52	0.9107	0.3619	0.943	1.382
410.60	0.9264	0.4133	0.938	1.387
415.35	0.9421	0.4833	0.940	1.378
420.20	0.9562	0.5632	0.942	1.371
425.04	0.9686	0.6505	0.941	1.366
429.55	0.9786	0.7419	0.943	1.335
438.15	1.0000	1.0000	1.000	-

calculated using the virial equation of state truncated after the second term, namely:

$$\phi_i = \exp \left[\left(p / RT \right) \left(2 \sum_j y_j B_{ij} - \sum_j \sum_k y_j y_k B_{jk} \right) \right] \quad (3)$$

The second virial coefficients, B_{ii} and B_{ij} , for the pure components and for the mixtures were calculated using the equation proposed by Tsonopoulos (1974).

The VLE values for the mixtures considered were consistent according to the point-to-point test proposed by Fredenslund *et al.* (1977), although as stated above certain changes were made in the calculations of the virial coefficients and the molar volumes of the pure components, v_i^L . All mixtures were inconsistent with the area test by Redlich Kister, however the Herington test gave a positive

Fig. 3 Representation of (a), (y_1-x_1) vs x_1 , and (b), T vs x_1 or y_1 for the mixtures (x_1 , butyl esters+ x_2 , propan-2-ol) and those from literature, (○), butyl methanoate; (□), butyl ethanoate; (▲), butyl propanoate; (◇), butyl nutanoate

consistency for the mixtures butyl methanoate or ethanoate with propan-2-ol. The composition, x_1 and y_1 , values and temperature, T , were fitted using the following polynomial function analogous to Eq. (1):

$$Q_k = z_1 z_2 \sum A_i \{z_1 / [z_1 + k(1 - z_1)]\}^i \quad (4)$$

where z is either x_i or y_i , depending on the case, and Q_k is the function to be fitted. **Table 4** presents the values of the parameters for Eq (4) and the standard deviation $s(Q_k)$, calculated by correlating the functions $Q_1 = (y_1-x_1)$, $Q_2 = T - \sum x_i T_{b,i}$, and $Q_3 = T - \sum y_i T_{b,i}$ on x_1 or, in the case of the last two functions, on y_1 . $T_{b,i}$ is the boiling temperature of pure component i . **Figures 3 (a, b)** plot the experimental and calculated values for (y_1-x_1) on x_1 and T on x_1 and y_1 , respectively, fitting the curves using Eq. (4). Our values showed good agreement with the values reported by Gmehling *et al.* (1982) for (butyl ethanoate+propan-2-ol), the only one of the systems considered here for which values were found in the literature. Only a single azeotrope was for all four of the systems considered, namely, a minimum azeotrope for (butyl methanoate+propan-2-ol). The azeotrope was calculated using the correlations for Q_1 , Q_2 , and Q_3 referred to above and the parameter values given in Table 4. The coordinates of the singular point were $x_1 = y_1 = 0.038$, $T = 354.9$ K. Lecat (see Gmehling *et al.*, 1994) postulated that there was no azeotrope for this mixture. Because the singular point is present at low butyl ester concentrations, for it to be reflected in the correlation of the function $Q_1 = y_1-x_1$, during fitting the linear regression had to be weighted statistically, such that the absolute

error between the experimental and calculated values over the interval $x_1 < 0.05$ was five and one-half times higher than over the remainder of the concentration range.

Figure 4 plots the equimolar values for (y_1-x_1) obtained for the various (alkyl ester+propan-2-ol) mixtures (unpublished data for certain mixtures) at 101.32 kPa under isobaric VLE conditions, according to ester type. The figure shows that the values were quite regular and that the regression lines had negative slopes.

3. Prediction of VLE Values Using Different Group-Contribution Models

The activity coefficient, γ_i , values and the vapor phase composition, y_i , values from Table 3 were compared to predictions calculated using ASOG group-contribution model (Tochigi *et al.*, 1990) and the various versions of the UNIFAC group-contribution model (Fredenslund *et al.*, 1975; Larsen *et al.*, 1987; and Gmehling *et al.*, 1993). The quantitative valuation of the results is reflected in **Table 5** for the different cases. On the whole, the modified UNIFAC model as proposed by Gmehling *et al.* (1993) yielded the best estimates of γ_i , with a mean estimation error of 4.3% for the four systems considered. The ASOG model yielded a mean error of 5.2% for these same four systems observing a variation of the mean error with the ester chain-length. The version of the UNIFAC model proposed by Larsen *et al.* (1987) could not be applied to the mixture of butyl methanoate+propan-2-ol, because no interaction parameter values were available for the HCOO

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

Correlation	k	A_0	A_1	A_2	A_3	$s(Q_k)$
Butyl Methanoate+Propan-2-ol						
Q_1 vs. x_1	1.343	0.078	-2.819	3.962	-4.262	0.003
Q_2 vs. x_1	1.07	-31.07	18.18	-54.91	-	0.13
Q_3 vs. y_1	0.19	-111.19	411.95	-698.53	402.64	0.15
Butyl Ethanoate+Propan-2-ol						
Q_1 vs. x_1	3.820	-0.545	-3.562	1.444	-3.247	0.001
Q_2 vs. x_1	2.61	-35.84	-50.06	-65.07	-	0.12
Q_3 vs. y_1	0.21	-41.92	104.23	-45.96	-	0.12
Butyl Propanoate+Propan-2-ol						
Q_1 vs. x_1	3.428	-0.702	-3.804	1.334	-5.150	0.001
Q_2 vs. x_1	1.59	-52.25	-38.50	-112.82	-	0.21
Q_3 vs. y_1	0.13	-58.38	270.48	-172.64	-	0.12
Butyl Butanoate+Propan-2-ol						
Q_1 vs. x_1	5.520	-0.878	-5.513	-1.318	-6.406	0.001
Q_2 vs. x_1	1.79	-70.21	-133.99	109.10	-308.61	0.30
Q_3 vs. y_1	0.09	-79.42	962.43	-1264.53	439.92	0.12

Fig 4 Variation of the experimental equimolar quantity ($y_1 - x_1$) as a function of the chain-length, u , of alkyl esters, $C_{u-1}H_{2u-1}COOR_1$ for the binary mixtures: (x_1 alkyl esters+ x_2 propan-2-ol). R_1 = methyl, ethyl, propyl, butyl

group. For the three remaining mixtures the mean error in the γ_i estimates was 8.6%. In general, the original version of UNIFAC also presents major discrepancies with the ester chain-length increases, and depending upon the interaction pair selected, the version of this model published by Fredenslund *et al.* (1975) yielded mean errors for γ_i of 4.6% for the interaction pair COH/COO and of 17.6% if the parameters more recent published (OH/HCOO, OH/COOC) are

Fig. 5 Differences, δy_1 , obtained in the prediction of the mixtures (x_1 butyl esters+ x_2 propan-2-ol) using different group-contribution models: ASOG (OH/COO, Tochigi *et al.*, 1990); UNIFAC (OH/HCOO, OH/COOC, Hansen *et al.*, 1991); UNIFAC (OH/COO, Macedo *et al.*, 1983); G-UNIFAC (OH/HCOO, OH/COOC, Gmehling *et al.*, 1993)

used, see columns 2 and 3 in Table 5.

The concentrations of the vapor phase, y_1 , were also estimated, using Eq. (2), and the differences with respect to the experimental values have been plotted on butyl ester concentration in **Fig. 5 (a-d)**. The predicted values for the last three mixtures considered were quite regular, though the differences turned excessive in the regions rich in ester. Of the different models considered, only the versions of the UNIFAC model as recently published by Hansen *et al.* (1991) and Gmehling *et al.* (1993) predicted an azeotrope for the mixture of (butyl methanoate+propan-2-ol). The estimated coordinate values for the singular point are shown

Table 5 Average percent errors, mean deviation, maximum deviation, and azeotropic data, obtained in the prediction of VLE for mixtures Butyl alkanoates+Propan-2-ol using different group-contribution models

	ASOG		UNIFAC		Mod. UNIFAC		
	OH/COO ⁽¹⁾	OH/COOC* ⁽²⁾	COH/COO ⁽³⁾	CCOH/COOC ⁽⁴⁾	OH/COO ⁽⁵⁾	OH/COOC ⁽⁶⁾	OH/COOC* ⁽⁷⁾
Butyl Methanoate (1)+2-Propanol (2)							
$\bar{e}(\gamma_i)$	2.1	9.4	5.8	-	2.2	-	2.3
$\bar{\delta}(y_i)$	0.010	0.009	0.015	-	0.008	-	0.005
$\delta_{max}(y_i)$ (at $x_1 =$)	0.023 (0.515)	-0.025 (0.256)	0.029(0.468)	-	0.017 (0.468)	-	0.013 (0.515)
Azeotrope (x_1 , T/K)	-	(0.020, 354.6)	-	-	-	-	(0.031, 354.8)
Butyl Ethanoate (1)+2-Propanol (2)							
$\bar{e}(\gamma_i)$	4.7	13.2	2.4	6.6	7.3	4.3	5.3
$\bar{\delta}(y_i)$	0.005	0.012	0.002	0.007	0.008	0.06	0.004
$\delta_{max}(y_i)$ (at $x_1 =$)	-0.010 (0.183)	-0.023 (0.353)	-0.008 (0.901)	-0.012 (0.527)	-0.012 (0.527)	-0.011 (0.183)	-0.008 (0.938)
Butyl Propanoate (1)+2-Propanol (2)							
$\bar{e}(\gamma_i)$	6.1	21.8	4.3	15.9	11.7	9.0	2.7
$\bar{\delta}(y_i)$	0.010	0.018	0.010	0.015	0.014	0.013	0.011
$\delta_{max}(y_i)$ (at $x_1 =$)	-0.030 (0.961)	-0.036 (0.961)	-0.030 (0.961)	-0.034 (0.961)	-0.034 (0.961)	-0.030 (0.961)	-0.033 (0.961)
Butyl Butanoate (1)+2-Propanol (2)							
$\bar{e}(\gamma_i)$	7.9	26.0	5.7	19.6	15.5	12.4	7.0
$\bar{\delta}(y_i)$	0.014	0.017	0.010	0.013	0.012	0.015	0.011
$\delta_{max}(y_i)$ (at $x_1 =$)	-0.037 (0.979)	-0.039 (0.979)	-0.029 (0.979)	-0.029 (0.979)	-0.029 (0.979)	-0.037 (0.979)	-0.033(0.979)

$$\bar{e}(\gamma_i) = \frac{2}{N} \sum_{i=1}^N \sum_{j=1}^N |(\gamma_{i,exp} - \gamma_{i,cal}) / \gamma_{i,exp}| \cdot 100 / N; \quad \bar{\delta}(y_i) = \frac{1}{N} \sum_{i=1}^N |y_{i,exp} - y_{i,cal}| / N; \quad \delta_{max}(y_i) = \max(y_{i,exp} - y_{i,cal})$$

* For the mixture butyl methanoate+2-propanol the interaction considered is OH/HCOO

1) Tochigi *et al.* (1990) 2) Hansen *et al.* (1991) 3) Fredensund *et al.* (1975) 4) Fredenslund *et al.* (1977) 5) Macedo *et al.* (1983)

6) Larsen *et al.* (1987) 7) Gmehling *et al.* (1993)

in Table 5 and both, but particularly that estimated by Gmehling *et al.* (1993), are in quite good agreement with the experimental value.

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Nomenclature

A_i	= coefficients in Eq. (4)	[-]
B_{ij}	= cross-virial coefficients	[m ³ kmol ⁻¹]
k	= parameter in Eq. (1)	[-]
N	= number of experimental points	[-]
p	= total pressure	[kPa]
p_i^0	= vapor pressure of pure component i	[kPa]
R	= universal gas constant	[JK ⁻¹ mol ⁻¹]
s	= standard deviation	[-]
T	= temperature	[K]
$T_{b,i}^0$	= boiling temperature of pure component i	[K]
$v_{i,i}^L$	= molar volume of pure component i	[m ³ kmol ⁻¹]
V_i	= coefficients in Eq. (1)	[-]
x	= liquid-phase molar fraction	[-]
y	= vapor-phase molar fraction	[-]

<Greek letters>

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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