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Isobaric Vapor−Liquid Equilibria of Methanol + Methyl Ethanoate, + Methyl Propanoate, and + Methyl Butanoate at 141.3 kPa

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Isobaric vapor−liquid equilibrium data at 141.3 kPa for the binary systems methanol + methyl ethanoate, +methyl propanoate, and +methyl butanoate are presented. All mixtures show positive deviations from ideality but only the mixtures methanol + methyl ethanoate and methanol + methyl propanoate show a minimum temperature azeotrope. The results are tested for thermodynamic consistency and correlated with several equations. The results are compared with the predictions of the ASOG and UNIFAC methods.

Introduction

For a number of years our laboratory has been pursuing a research project investigating the vapor−liquid equilibria for mixtures consisting of alkyl esters and normal or isomeric alkanols at different pressures. Previous papers (Ortega *et al*., 1986; Susial *et al*., 1989; Ortega *et al*., 1990a,b; Ortega and Susial 1993) have reported VLE results for mixtures of methyl esters and normal alkanols other than methanol, which we decided to consider separately. In the present study VLE measurements were made for binary systems consisting of methanol and the first methyl esters (ethanoate, propanoate, and butanoate) at a constant pressure of 141.3 kPa. The literature contains several isobaric VLE studies for the mixture comprising methanol (1) + methyl ethanoate (2) at different pressures [26.7 kPa, Balashov *et al*. (1967), see Gmehling *et al*. (1977); 101.3 kPa, Mato and Cepeda (1984), see Gmehling *et al*. (1988); 585.5 kPa, Nagahama and Hirata (1971), see Gemhling *et al*. (1977)], though no study is made at the same pressure employed herein. Except the values for the azeotropic coordinates published by Horsley (1973) and Gmehling *et al*. (1994), which have been included for the purpose of comparison, no values for the other mixtures have been found.

Finally, as in previous papers, we have considered the usefulness of certain group-contribution models for mixtures containing methanol and have assessed the goodness of the predictions obtained using the models with a single interaction group specifically for that alkanol.

Experimental Section

1. Components. Both methanol and the methyl esters were supplied by Fluka. The components were first degassed using ultrasound for several hours and then dried on a molecular sieve (Fluka, 0.3 nm) to remove all possible traces of moisture before use, but no other treatments were applied. In order to verify the purity of the components, such physical properties as density, ρ, refractive index, n(D,298.15 K) and normal boiling point, $T^{\circ}_{b,i}$, at 101.32 kPa were measured. Table 1 compares our values with the literature. Our experimental values show good agreement with those reported by other workers, except for a difference of 1 K in the boiling point of methyl propanoate with respect to the value published by TRC (1993), though the experimental value was practically identical to the temperature recorded by us some time ago (Susial *et al*., 1989), probably due to the high purity of the ester employed by us.

Table 1. Physical Properties of the Pure Compounds Supplied by Fluka at Atmospheric Pressure

	$T^{\circ}_{b,i}$/K		ρ(298.15 K)/kg·m^{-3}		n(D, 298.15)	
purity/%	exp	lit.	exp	lit.	exp	lit.
			Methyl Ethanoate			
>99.5	329.87	330.018^{a} 330.09^{b} 329.82^{c}	927.01	927.90^{a} 927.30^{b} 926.99^{c}	1.3589	1.3589^{a,b} 1.3593^{c}
			Methyl Propanoate			
>99.0	351.55	352.60^{b} 351.65^{d}	909.35	909.00^{b} 908.53^{d}	1.3745	1.3742^{b} 1.3740^{d}
			Methyl Butanoate			
>99.0	375.24	375.90^{b} 375.30^{e}	892.26	892.61^{b} 892.37^{e}	1.3852	1.3845^{b} 1.3851^{e}

[a] Riddick *et al*. (1986). [b] TRC (1993). [c] Ortega *et al*. (1990b). [d] Susial *et al*. (1989). [e] Ortega *et al*. (1990a).

2. Equipment and Procedure. The experimental equipment used to achieve the isobaric VLE measurements was the same employed in previous work, already described by Ortega *et al*. (1986); however, certain alterations were made in order to be able to work at higher pressures, including new electronics for the Fisher model VK1 pressure controller, whose precision was ±0.2 kPa. The equilibrium temperature was measured with an ASL model F25 digital platinum-resistance thermometer to a precision of ±0.01 K.

The concentrations of the liquid and vapor phases at equilibrium were analyzed using an Anton Paar model DMA-55 digital densimeter on the basis of standard density−composition curves obtained previously for each of the binary systems at (298.15 ± 0.01) K. The precision of the calculations was less than ±0.002 units for both phases.

Experimental Results

Table 2 presents the experimental $T-x_1-y_1$ VLE values for the three systems considered at the working pressure of (141.3 ± 0.2) kPa. The table also gives the values of the activity coefficients, γ_i, for both the components in the liquid phase, calculated using the expression

$$\ln \gamma_i = \ln\left(\frac{py_i}{p_i^{\circ}x_i}\right) + \frac{(B_{ii}v_i^{L})(p - p_i^{\circ})}{RT} + \frac{P}{2RT}\sum_j\sum_k y_j y_k(2\delta_{ji} - \delta_{jk}) \quad (1)$$

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Table 2. Experimental VLE Data for the Binary Systems Methanol (1) + Methyl Alkanoates (2) at 141.3 kPa

T/K	x_1	y_1	γ_1	γ_2
Methanol (1) + Methyl Ethanoate (2)				
339.38	0.000	0.000		1.000
338.40	0.041	0.077	2.487	0.999
337.71	0.074	0.122	2.257	1.006
337.05	0.110	0.170	2.155	1.011
336.47	0.142	0.211	2.122	1.015
336.02	0.187	0.253	1.960	1.029
335.66	0.248	0.297	1.760	1.059
335.40	0.296	0.332	1.666	1.083
335.37	0.384	0.381	1.473	1.149
335.47	0.442	0.414	1.387	1.197
335.73	0.517	0.450	1.276	1.287
336.30	0.613	0.499	1.167	1.437
336.89	0.679	0.540	1.117	1.558
337.71	0.745	0.588	1.075	1.713
338.35	0.785	0.622	1.053	1.828
339.20	0.824	0.666	1.039	1.931
340.35	0.870	0.722	1.024	2.084
341.65	0.910	0.785	1.014	2.251
342.79	0.937	0.838	1.009	2.338
344.03	0.965	0.900	1.006	2.485
345.25	0.987	0.963	1.007	2.420
345.92	1.000	1.000	1.000	
Methanol (1) + Methyl Propanoate (2)				
361.38	0.000	0.000		1.000
359.02	0.024	0.068	1.819	1.043
355.55	0.070	0.183	1.879	1.066
352.75	0.123	0.296	1.919	1.060
350.89	0.169	0.371	1.862	1.060
349.34	0.214	0.430	1.797	1.065
347.85	0.282	0.492	1.641	1.092
346.60	0.349	0.545	1.538	1.121
345.73	0.423	0.590	1.415	1.174
345.12	0.489	0.626	1.330	1.230
344.72	0.552	0.658	1.253	1.304
344.34	0.642	0.695	1.155	1.470
344.12	0.699	0.732	1.127	1.545
344.06	0.738	0.750	1.095	1.664
344.06	0.782	0.775	1.068	1.794
344.15	0.829	0.806	1.044	1.969
344.32	0.868	0.835	1.026	2.166
344.51	0.902	0.867	1.018	2.345
344.79	0.927	0.894	1.011	2.493
345.06	0.951	0.923	1.008	2.678
345.40	0.971	0.952	1.007	2.731
345.70	0.985	0.974	1.005	2.786
345.92	1.000	1.000	1.000	
Methanol (1) + Methyl Butanoate (2)				
386.41	0.000	0.000		1.000
383.94	0.016	0.086	1.632	0.990
380.65	0.040	0.190	1.591	0.984
377.83	0.060	0.266	1.599	0.986
373.68	0.091	0.368	1.665	0.990
369.63	0.120	0.450	1.732	1.005
366.79	0.146	0.508	1.760	1.010
363.19	0.186	0.576	1.747	1.021
358.59	0.251	0.656	1.715	1.042
356.91	0.290	0.685	1.634	1.065
352.80	0.408	0.761	1.483	1.110
351.53	0.470	0.782	1.380	1.183
350.60	0.520	0.800	1.317	1.233
349.67	0.577	0.821	1.258	1.297
349.02	0.621	0.836	1.217	1.354
348.64	0.655	0.849	1.187	1.388
347.75	0.740	0.873	1.116	1.594
347.30	0.811	0.894	1.058	1.864
346.83	0.862	0.916	1.036	2.075
346.51	0.911	0.935	1.014	2.486
346.39	0.933	0.947	1.006	2.708
346.23	0.967	0.971	1.000	3.106
346.13	0.983	0.984	1.001	3.321
345.92	1.000	1.000	1.000	

where

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \tag{2}$$

Table 3. Correlation Parameters and Standard Deviations, $s(Q_0)$, Obtained Using Different Equations, $Q_0 = G^E/(J\ mol^{-1})$

eq	parameters	$s(Q_0)$
Methanol (1) + Methyl Ethanoate (2)		
Van Laar	$A_{12} = 0.967$, $A_{21} = 1.024$	5.5
Margules	$A'_{12} = 0.967$, $A'_{21} = 1.023$	5.5
Wilson	$\Delta\lambda_{12} = 3377.0$ J mol^{-1}, $\Delta\lambda_{21} = -135.9$ J mol^{-1}	5.2
NRTL ($\alpha = 0.47$)	$\Delta g_{12} = 1828.6$ J mol^{-1}, $\Delta g_{21} = 1385.5$ J mol^{-1}	5.5
UNIQUAC ($Z = 10$)	$\Delta u_{12} = -250.3$ J mol^{-1}, $\Delta u_{21} = 2463.1$ J mol^{-1}	5.6
Redlich−Kister	$A_0 = 0.992$, $A_1 = -0.008$, $A_2 = 0.017$, $A_3 = 0.091$	3.7
eq 3 ($k = 1.532$)	$A_0 = 0.945$, $A_1 = 0.360$, $A_2 = -0.871$, $A_3 = 0.687$	3.6
Methanol (1) + Methyl Propanoate (2)		
Van Laar	$A_{12} = 1.045$, $A_{21} = 1.007$	41.1
Margules	$A'_{12} = 1.043$, $A'_{21} = 1.009$	41.1
Wilson	$\Delta\lambda_{12} = 4553.4$ J mol^{-1}, $\Delta\lambda_{21} = -1090.3$ J mol^{-1}	40.9
NRTL ($\alpha = 0.47$)	$\Delta g_{12} = 1511.1$ J mol^{-1}, $\Delta g_{21} = 1915.3$ J mol^{-1}	41.0
UNIQUAC ($Z = 10$)	$\Delta u_{12} = -640.5$ J mol^{-1}, $\Delta u_{21} = 3340.0$ J mol^{-1}	43.0
Redlich−Kister	$A_0 = 0.961$, $A_1 = 0.093$, $A_2 = 0.366$, $A_3 = -0.337$	22.5
eq 3 ($k = 0.143$)	$A_0 = 2.887$, $A_1 = -4.793$, $A_2 = 2.999$	10.1
Methanol (1) + Methyl Butanoate (2)		
Van Laar	$A_{12} = 0.746$, $A_{21} = 1.261$	39.5
Margules	$A'_{12} = 0.678$, $A'_{21} = 1.217$	35.8
Wilson	$\Delta\lambda_{12} = 3406.4$ J mol^{-1}, $\Delta\lambda_{21} = 245.0$ J mol^{-1}	35.8
NRTL ($\alpha = 0.47$)	$\Delta g_{12} = 3325.0$ J mol^{-1}, $\Delta g_{21} = 292.1$ J mol^{-1}	38.2
UNIQUAC ($Z = 10$)	$\Delta u_{12} = -144.3$ J mol^{-1}, $\Delta u_{21} = 2459.1$ J mol^{-1}	35.2
Redlich−Kister	$A_0 = 0.985$, $A_1 = 0.034$, $A_2 = -0.190$, $A_3 = 0.541$	19.4
eq 3 ($k = 0.312$)	$A_0 = -0.522$, $A_1 = 6.022$, $A_2 = -8.622$, $A_3 = 4.299$	7.1

Table 4. Coefficients A_i and k and Standard Deviations, $s(Q_k)$, Obtained with Eq 3 for $Q_1 = (y_1 - x_1)$ and $z = x_1$, Q_2 (K) $= (T - \sum x_i T^\circ_{b,i})$ and $z = x_1$, and Q_3 (K) $= (T - \sum y_i T^\circ_{b,i})$ and $z = y_1$

	k	A_0	A_1	A_2	A_3	A_4	$s(Q_k)$
Methanol (1) Methyl Ethanoate (2)							
Q_1	1.26	0.975	−4.290	5.316	−4.099		0.002
Q_2 (K)	1.33	−34.51	40.16	−58.26			0.04
Q_3 (K)	0.50	−11.26	−67.08	69.18			0.07
Methanol (1) + Methyl Propanoate (2)							
Q_1	1.43	2.090	−6.305	7.970	−4.631		0.003
Q_2 (K)	0.59	−91.04	198.07	−318.97	333.09	−157.18	0.04
Q_3 (K)	0.58	−15.53	−78.33	377.01	−650.29	342.02	0.02
Methanol (1) + Methyl Butanoate (2)							
Q_1	0.95	4.383	−11.860	14.570	−7.083		0.002
Q_2 (K)	0.30	−87.85	−214.92	523.80	−259.56		0.04
Q_3 (K)	0.82	5.94	49.82	−98.72			0.07

The vapor pressures, p_i°, were calculated using the Antoine equation with the constant values published in previous papers. For methanol the values were from Blanco and Ortega (in press); for methyl ethanoate and propanoate the values were from Ortega and Susial (1993), and for methyl butanoate they were from Ortega *et al.* (1990a). The empirical correlation proposed by Tsonopoulos (1974) was used to determine the values of the virial coefficients, B_{ij}, and Rackett's equation as modified by Spencer and Danner (1972) was used to calculate the molar volumes, v_i^L. The thermodynamic consistency of the data was evaluated using the point-to-point test modified as described above, and all the mixtures displayed positive consistency. The term for the heat of mixing, $(\Delta h/RT^2)$-

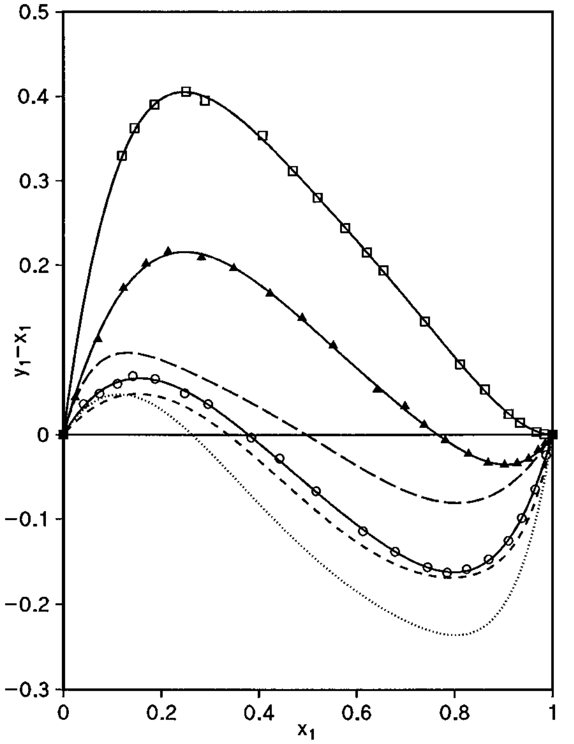

Figure 1. Experimental points and curves of $(y_1 - x_1)$ *vs* x_1 for the mixtures of methanol (1) with methyl ethanoate (○), methyl propanoate (▲), and methyl butanoate (□). Curves represent the literature values for methanol (1) + methyl ethanoate (2) at different pressures: (···) 26.7 kPa; (- - -) 101.3 kPa; (— — —) 585.5 kPa (see, respectively, Gmehling et al. (p 91, 1977; p 78, 1988; p 104, 1977)).

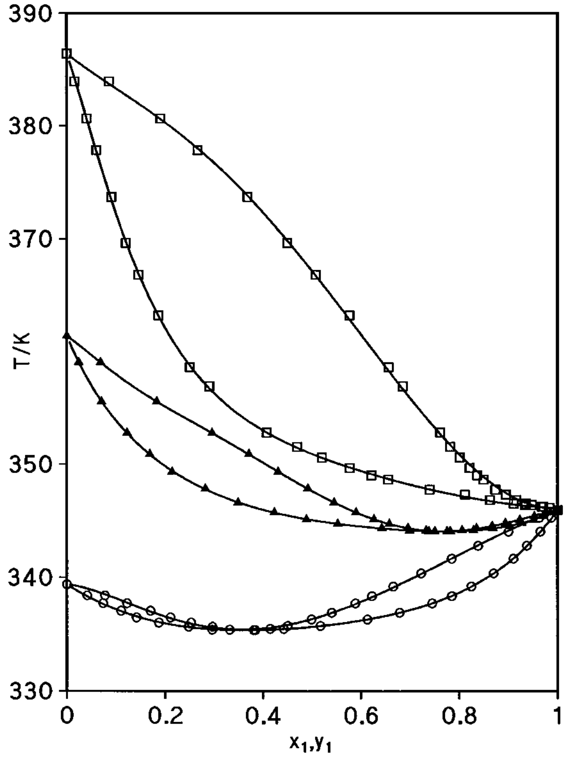

Figure 2. Experimental points and curves of T *vs* x_1 or y_1 for the mixtures of methanol (1) with methyl ethanoate (○), methyl propanoate, (▲), and methyl butanoate, (□).

$(dT/dx_1)_p$, was only considered for the system consisting of methanol (1) + methyl ethanoate (2), using the enthalpy values published by Nagata *et al.* (1972), though the influence of that term turned out to be virtually negligible.

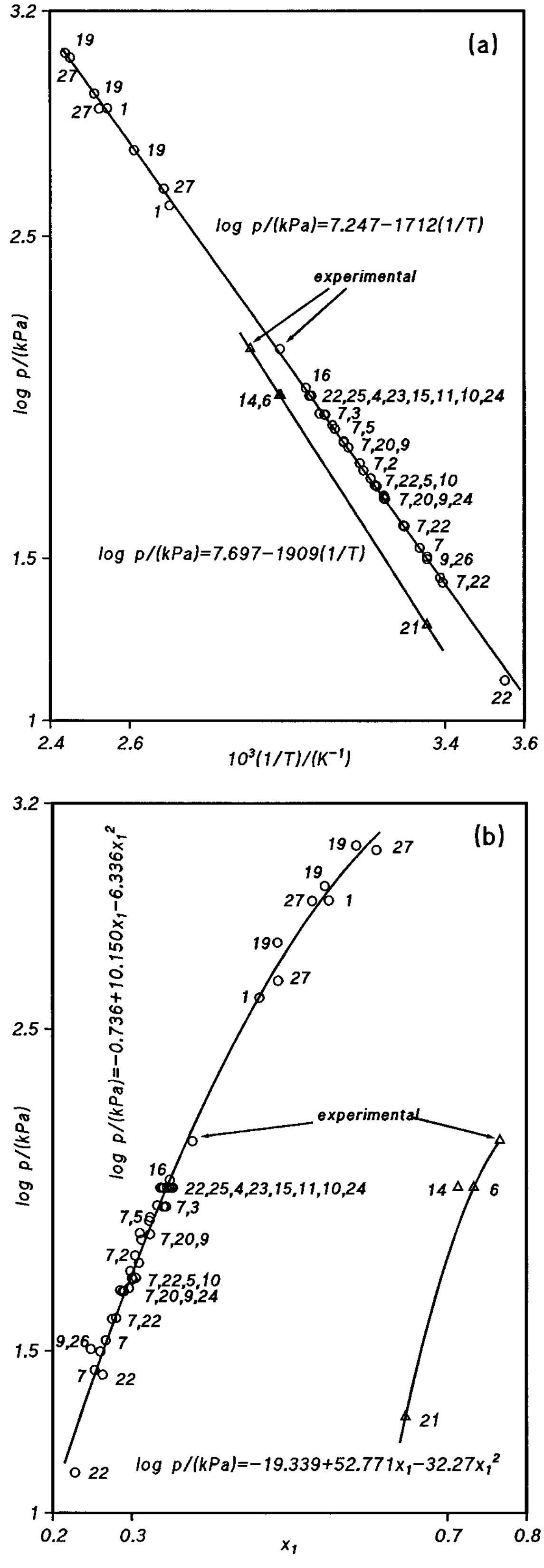

Figure 3. Representation of (a) log p *vs* $(1/T)$ and (b) log p *vs* x_1 for the azeotropic points of the mixtures of methanol (1) with methyl ethanoate (○) and methyl propanoate (△) and the corresponding correlation curves. Key: (1−5, 7−13, 15−20, 22−25) Gmehling et al. (1994), pp 122−123; (14, 21) Gmehling et al. (1994), p 129; (27) Horsley (1973), p 76; (6) Horsley (1973), p 78; (26) Martín et al. (1994).

For the other systems no heat of mixing values were found in the literature. The test proposed by Redlich−Kister (1948), Herington (1951), and recently Wisniak (1994), this

Table 5. Average Errors Calculated in the Prediction of VLE Data and Azeotropic Values Estimated Using the ASOG and UNIFAC Models

	ASOG	UNIFAC		mod UNIFAC	
	OH/COO[a]	CH_3OH/COO[b]	CH_3OH/COOC[c]	CH_3OH/COOC[d]	CH_3OH/COOC[e]
	Methanol (1) + Methyl Ethanoate (2)				
$\bar{e}(y_1)^f$	4.2	5.7	2.1	5.1	2.2
$\bar{e}(\gamma_i)^g$	3.7	6.2	2.0	4.5	2.1
azeotrope (exp = 0.379)	0.435	0.325	0.377	0.400	0.375
	Methanol (1) + Methyl Propanoate (2)				
$\bar{e}(y_1)$	4.9	17.1	7.7	9.1	7.5
$\bar{e}(\gamma_i)$	3.1	16.7	8.6	6.9	7.4
azeotrope (exp = 0.766)	0.772	0.640	0.693	0.834	0.721
	Methanol (1) + Methyl Butanoate (2)				
$\bar{e}(y_1)$	4.1	21.0	9.8	8.4	10.9
$\bar{e}(\gamma_i)$	4.2	26.9	15.0	10.9	10.4
azeotrope (exp = nonazeotrope)	0.964	0.889	0.967	0.958	

[a] Tochigi *et al.*, 1990. [b] Macedo *et al.*, 1983. [c] Fredenslund *et al.*, 1977. [d] Larsen *et al.*, 1987. [e] Gmehling *et al.*, 1993. [f] $\bar{e}(y_1) = (1/N) \sum_{i=1}^{N} |(y_{ex} - y_{ca})/y_{exp}|100$. [g] $\bar{e}(\gamma_i) = (1/2) \sum_{j=1}^{2} \bar{e}(\gamma_j)$.

last-mentioned version including a term for enthalpies under isobaric equilibrium conditions, were also applied. All the three binary systems considered presented positive consistencies using the version of Herington (1951), whereas the other two versions yielded negative results for all the systems.

Treatment of VLE Values

The values of γ_i from Table 2 were used to calculate the Gibbs free energy, G^E, values, which were correlated with the mole fraction, x_1, of methanol using the equations proposed by van Laar, Margüles, Wilson, NRTL, UNIQUAC, and Redlich−Kister and a polynomial equation, similar to eq 3, written in a generic form with a variable z, that differed in each case. Using this function, it was possible to fit distributions of values which, like excess magnitudes, begin and end at the same value on the ordinate axis. Table 3 lists the coefficient values for the fits of g^E *vs* x_1, together with the standard deviations, for each of the above-mentioned equations and shows that the best results were achieved using equations with power series. Accordingly, eq 3 was used to correlate the other VLE magnitudes.

$$Q_k = z(1 - z)\sum A_i\{z/[z + k(1 - z)]\}^i \qquad (3)$$

where Q_k is the function to be correlated, namely, $Q_o = G^E$, $Q_1 = y_1 - x_1$, $Q_2 = T - \sum x_i T^{\circ}_{b,i}$, $Q_3 = T - \sum y_i T^{\circ}_{b,i}$, and $z = x_1, y_1$. T is the equilibrium temperature, and $T^{\circ}_{b,i}$ is the boiling point temperature for pure component i. Table 4 gives the parameters for the correlations of composition and temperature using eq 3. The experimental values and the correlation curves for ($y_1 - x_1$) *vs* x_1 for the mixtures considered at 141.3 kPa are plotted in Figure 1. The figure also presents curves for the mixture composed of methanol (1) + methyl ethanoate (2) at different pressures for qualitative comparison with our values. Figure 2 presents the equilibrium values for T *vs* x_1 or y_1 from Table 2 for the mixtures considered here, together with the corresponding fitting curves.

At the working pressure of 141.3 kPa, only the mixtures containing methyl ethanoate and methyl propanoate presented minimum azeotropes. The following coordinates were calculated using the relations described above: for methanol (1) + methyl ethanoate (2), $x_1 = y_1 = 0.377$, $T = 335.4$ K; and for methanol (1) + methyl propanoate (2) $x_1 = y_1 = 0.766$, $T = 344.0$ K. These values did not differ significantly from the values found by graphic interpolation. Horsley (1973) and Gmehling *et al.* (1994) found a total of 70 references in the literature dealing with the location of the singular point for the system methanol (1) + methyl ethanoate (2) under different conditions of temperature and pressure (ranging from 13.33 to 1172 kPa). In contrast, for the mixture methanol (1) + methyl propanoate (2) those same workers found only three values, none of which were at the working pressure used in this study. Figure 3a,b presents the plots for the magnitudes (log p) *vs* (1/T) and (log p) *vs* (x_1) comparing the location of the azeotropes calculated by us and those taken from the literature. There was acceptable agreement between the values reported by other researchers at other working

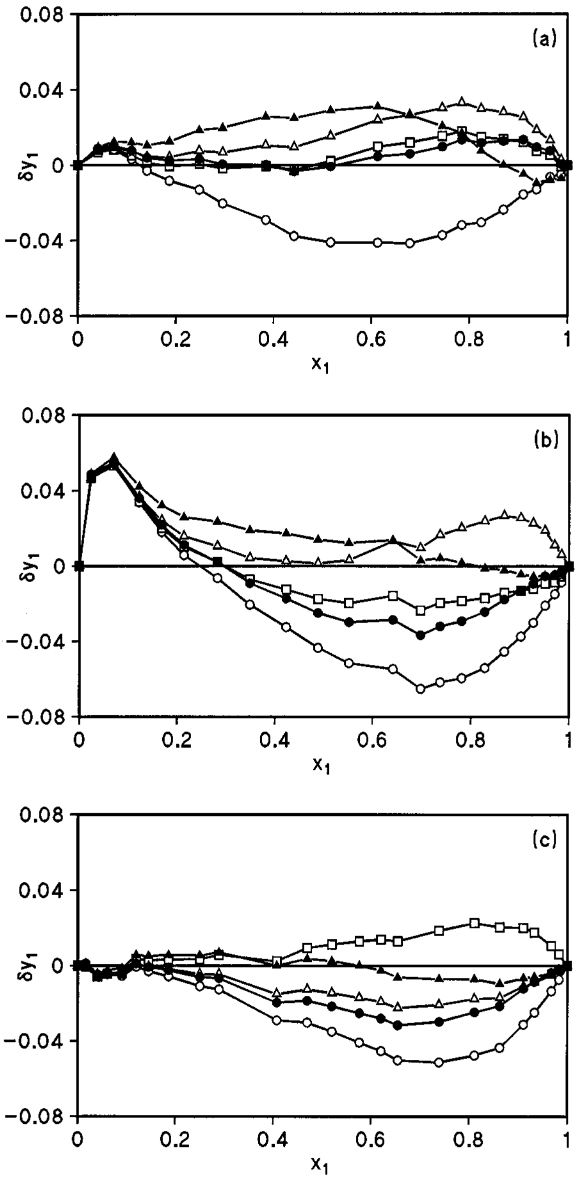

Figure 4. Deviations, $\delta y_1 = (y_{1,\,cal} - y_{1,\,exp})$, between estimated and experimental values using different group contribution models for methanol (1) + methyl alkanoates (2): ASOG (Tochigi *et al.*, 1990), (OH/COO) (▲); orig-UNIFAC (Macedo *et al.*, 1983), (CH_3-OH/COO) (○); (Fredenslund *et al.*, 1977), (CH_3OH/COOC) (●); mod-UNIFAC (Larsen *et al.* 1987), (CH_3OH/COOC) (△); (Gmehling *et al.*, 1993), (CH_3OH/COOC) (□); (a) methyl ethanoate; (b) methyl propanoate; (c) methyl butanoate.

pressures. The figure also depicts the correlations for the magnitudes employed, which yielded excellent estimates of the coordinates of the azeotropes for the two mixtures considered.

Prediction of VLE Using Group-Contribution Models

The experimental VLE values at 141.3 kPa were also compared to the values predicted by the ASOG group-contribution model (Tochigi *et al.* 1990) and by various versions of the UNIFAC group-contribution model (Fredenslund *et al.*, 1977; Larsen *et al.*, 1987; Gmehling *et al.*, 1993). The OH/COO group was used to represent the methanol/ester interaction in the ASOG model, while the UNIFAC model contemplated one group and specific interaction for methanol; either CH_3OH/COO or CH_3OH/COOC was used. The predictions achieved using each of the models were evaluated on the basis of the estimation error in the values of both the activity coefficients, γ_i, and the mole fraction of the vapor phase, y_1, and the results are presented in Table 5 together with the concentrations, $x_1 = y_1$, predicted for the azeotropes in each system. The version of the UNIFAC model of Gmehling *et al.* (1993) was the only model that predicted no azeotrope for the mixture consisting of methanol + methyl butanoate.

In general, the estimates for all three systems combined achieved using the ASOG model were better than the estimates achieved using any of the versions of the UNIFAC model. The ASOG model yielded a mean error of less than 5% in the predictions of the values of γ_i. For the UNIFAC model, the original version of Fredenslund *et al.* (1977) yielded better results when CH_3OH/CCOO was used as the interaction pair. The predictive ability of the model worsened with ester chain length, with mean errors of less than 5% for the mixture containing methyl ethanoate and up to 15−25% for the mixture containing methyl butanoate. The commun characteristic for all mixtures is the major discrepancy in the regions rich in methanol (see Figure 4a−c), except with the ASOG method whose estimations appear to be more regular.

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