VLE AT 114.66 AND 127.99 kPa FOR THE SYSTEMS METHYL ACETATE + ETHANOL AND METHYL ACETATE + PROPAN-1-OL. MEASUREMENTS AND PREDICTION

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Isobaric vapor-liquid equilibrium data at two pressures (114.66 and 127.99 kPa) over the entire range of compositions were obtained by using a recirculating equilibrium still for the binary systems formed by methyl acetate and either ethanol or propan-1-ol. In all cases, the systems studied exhibit positive deviations from ideal solution behavior. Methyl acetate + ethanol system shows an azeotrope at 114.66 kPa of $x = y = 0.954$ and $T = 333.4$ K and $x = y = 0.948$ and $T = 336.7$ K at 127.99 kPa. Once thermodynamic consistency was verified, prediction of data by several methods was carried out. Good predictions were obtained for all systems by the UNIFAC and ASOG methods, with mean error of about 5% as expected, but the calculated values for activity coefficients using the modified UNIFAC showed higher deviations.

Introduction

This paper is one of a series[12,13,14,17] dealing with isobaric vapor-liquid equilibria of mixtures composed of methyl esters and *n*-alkanols. An earlier paper[14] presented data for binary systems composed of methyl acetate/ethanol and methyl acetate/propan-1-ol at 101.32 kPa (760 Torr), indicating that, for the system methyl acetate(1) + ethanol(2), an azeotrope not previously recorded in the experimental data published in the literature,[4] although it had been predicted by Horsley,[7] was formed at $x_1 = 0.958$ and $T = 329.8$ K. The collection of data for other equilibrium conditions (see ref. 12) enables us to observe the evolution of the said system, methyl acetate(1) + ethanol(2), indicating changes in the composition of the azeotrope, a datum of considerable importance in the purification of chemical substances as well as in interpreting the thermodynamic behavior of the mixture by one of the theoretical models applied for that purpose.

In the above-mentioned series of papers, the ASOG and UNIFAC predictive methods were tested to verify the applicability of these models to ester/alkanol systems; and different interaction group pairs were considered with the UNIFAC model, in order to obtain the best approximation of the model to the behavior of the systems studied. The papers published to date do not provide an adequate basis for a comprehensive evaluation allowing one or the other of these models to be definitely recommended. Nevertheless, these models have been proven capable of estimating the activity coefficients with a quantitative precision of around 5%. In addition to applying the models mentioned above, the present study employs another version of the UNIFAC model, proposed by Larsen *et al.*,[9] which has not often been used to predict isobaric VLE data.

1. Experimental Section

The properties of the chemicals used in the study have been described in earlier papers.[14,17]

Measurements of the pure component vapor pressures and other experimental data on isobaric equilibrium states were taken, using a vapor-recirculating equilibrium still. The equipment and experimental procedure have already been described.[17] The composition of the samples of the vapor phase and the liquid phase removed from the experimental equipment after equilibrium had been attained was determined by densitometry using correlations obtained earlier for the excess molar volumes.[11] The estimated error in calculation of the mole fractions was ±0.001 for the liquid phase and slightly higher, around ±0.002, for the vapor phase, because of the volatile nature of methyl acetate.

2. Results and treatment of VLE data

The experimental vapor pressure values for the pure components, or their corresponding empirical correlations, have an important effect in the analysis of vapor-liquid equilibrium data. For this reason, the

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data (T, p_i°) for the n-alkanols were published in a previous paper[13] and **Table 1** presents the experimental temperature and vapor pressure for the methyl acetate. In all cases, the expression used to fit the experimental data was the Antoine equation:

$$\log p_i^\circ = A - B/(T-C) \qquad (1)$$

in which the parameters A, B and C were calculated by use of the nonlinear regression procedure of Nelder and Mead.[10] When fitted by Eq. (1), the data yielded the constant values given in **Table 2**.

The experimental $T-x_1-y_1$ data on the equilibrium vapor and liquid phases for the systems methyl acetate(1)+ethanol(2) and methyl acetate(1)+propan-1-ol(2) at pressures of 114.66±0.02 kPa (860±0.15 Torr) and 127.99±0.02 kPa (960±15 Torr) are set out in **Table 3**. Once the equilibrium compositions of the systems had been determined, the activity coefficients for the liquid phase (also given in Table 3) were calculated with the equation

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

where

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

The second virial coefficients for the pure components and the mixtures were determined by use of the empirical correlations proposed by Tsonopoulos.[18] The mixing parameters were calculated by use of the expressions given by Tsonopoulos[18] and the the values of k_{ij} for the mixtures were optimized in order to minimize the overall mean deviation in the mole fraction of the vapor phase, which was less than 0.01. In other words, in addition to applying the point-to-point test suggested by Fredenslund *et al.*,[2] with positive results in all cases, the subroutine of Hayden and O'Connell[5] for calculating the B_{ij} values was replaced by the empirical relations of Tsonopoulos.[18] The variation of k_{ij} produced a slight improvement in the final test results, decreasing the overall mean deviation of the mole fraction, y_1. In any event, the variations in k_{ij} did not significantly affect the results for δy_1, although the best values fluctuated around $k_{ij}=0.3$—substantially different from the value of 0.05 suggested by Tsonopoulos[18] when one of the components is an n-alkanol. For all the systems studied, Tsonopoulos's[18] version of the consistency test produced better results ($\delta y_1 \ll 0.01$) than did the test described by Fredenslund *et al.*,[2] but the results were positive in all cases. Similarly, Herington's[6] test of areas was always positive as well.

Table 1. Vapor pressures of methyl acetate obtained experimentally

Temperature (K)	Vapor pressure p_i°/(kPa)	Temperature (K)	Vapor pressure p_i°/(kPa)
306.80	42.45	326.44	90.16
307.51	43.72	327.39	93.23
308.28	45.15	328.40	96.64
308.75	46.00	329.30	99.73
309.02	46.49	330.37	103.49
310.46	49.28	331.18	106.44
310.56	49.50	332.12	109.92
311.87	52.15	332.95	113.11
312.48	53.42	333.73	116.15
312.98	54.48	334.70	120.00
313.70	56.05	335.48	123.17
314.23	57.22	336.28	126.54
315.61	60.38	337.04	129.79
316.96	63.58	337.84	133.23
318.44	67.27	338.41	135.77
319.54	70.10	339.33	139.93
320.82	73.50	340.01	143.12
321.70	75.92	340.88	147.30
323.10	79.94	341.32	149.42
324.15	83.03	341.96	152.54
325.32	86.62	342.54	155.42

Table 2. Antoine constants and standard deviations, $s(p_i^\circ)$, fro pure compounds

Compound	Ref.	A	B	C	$s(p_i^\circ)$ (kPa)
Methyl Acetate	this work	6.4934	1329.46	33.52	0.04
	(15)	6.2441	1183.70	50.74	
Ethanol	(13)	7.1130	1513.02	55.15	0.02
	(15)	7.1688	1552.60	50.73	
Propan-1-ol	(13)	6.8698	1434.94	74.98	0.04
	(15)	6.8761	1441.70	74.29	

Reduction of the equilibrium data was performed with a polynomial equation of the form

$$Q = x_1 x_2 \sum_{i=0}^{m} A_i [x_1/(x_1 + k x_2)]^i \qquad (4)$$

where x_1 is the mole fraction of the methyl acetate and m is the number of parameters A_i. The number of parameters A_i was not set beforehand; instead, the lowest degree that yielded the best reduction of the VLE data in the least-squares procedure employed was chosen. The correlation of the data obtained using Eq. (4) was optimized, taking the standard deviation, $s(Q)$, as the objective function. The parameter k played an important role in the optimization; minimization of the objective function was carried out by varying the value of k in the polynomial of given degree. The value of k was always positive, because if $k<0$ the term in brackets in Eq. (4) would show a discontinuity at $x_1 = k/(k-1)$.

Thus, the parameters of Eq. (4) were obtained for $Q = g^E/RT$, and the values are shown in **Table 4**,

Table 3. Vapor-Liquid data and activity coefficiens for the systems methyl acetate(1) + ethanol(2) and methyl acetate(1) + propan-1-ol at 114.66 and 127.99 kPa

p/kPa	T/K	x_1	y_1	γ_1	γ_2
	x_1Methyl Acetate + x_2Ethanol				
114.66	352.50	0.0217	0.0873	2.278	1.007
	351.73	0.0314	0.1217	2.243	1.008
	349.40	0.0650	0.2217	2.110	1.012
	348.28	0.0838	0.2666	2.032	1.016
	347.18	0.1046	0.3117	1.966	1.019
	346.40	0.1215	0.3424	1.902	1.023
	344.72	0.1603	0.4071	1.801	1.031
	342.95	0.2019	0.4653	1.724	1.051
	342.22	0.2272	0.4911	1.653	1.064
	341.63	0.2419	0.5091	1.639	1.071
	340.90	0.2664	0.5301	1.584	1.092
	340.20	0.2961	0.5570	1.530	1.104
	339.72	0.3184	0.5753	1.492	1.115
	339.13	0.3465	0.5946	1.443	1.137
	338.63	0.3750	0.6133	1.397	1.158
	338.10	0.4086	0.6320	1.343	1.191
	337.46	0.4459	0.6559	1.303	1.221
	337.01	0.4740	0.6715	1.273	1.251
	336.72	0.4953	0.6821	1.249	1.277
	336.38	0.5220	0.6964	1.223	1.306
	336.09	0.5489	0.7089	1.195	1.344
	335.76	0.5752	0.7221	1.174	1.381
	335.41	0.6068	0.7382	1.150	1.427
	335.11	0.6366	0.7531	1.129	1.475
	334.90	0.6579	0.7638	1.116	1.512
	334.70	0.6844	0.7765	1.098	1.564
	334.47	0.7105	0.7906	1.084	1.613
	334.20	0.7436	0.8080	1.068	1.690
	334.10	0.7651	0.8203	1.057	1.734
	333.95	0.7862	0.8327	1.050	1.785
	333.90	0.8026	0.8427	1.042	1.821
	333.68	0.8377	0.8644	1.032	1.928
	333.61	0.8583	0.8786	1.026	1.983
	333.48	0.8819	0.8953	1.022	2.063
	333.45	0.9025	0.9109	1.017	2.129
	333.43	0.9195	0.9244	1.013	2.190
	333.42	0.9326	0.9350	1.011	2.250
	333.40	0.9430	0.9439	1.010	2.298
	333.38	0.9594	0.9592	1.009	2.348
	333.41	0.9680	0.9673	1.008	2.385
	333.43	0.9770	0.9759	1.007	2.443
	333.50	0.9929	0.9920	1.005	2.619
127.99	355.35	0.0291	0.1034	2.066	0.996
	352.00	0.0780	0.2485	2.034	0.996
	350.55	0.1078	0.3095	1.910	1.000
	348.90	0.1368	0.3652	1.862	1.012
	347.55	0.1693	0.4191	1.795	1.014
	346.35	0.2017	0.4601	1.713	1.028
	345.20	0.2371	0.4989	1.635	1.045
	344.25	0.2717	0.5321	1.565	1.061
	343.45	0.2965	0.5559	1.535	1.077
	342.43	0.3438	0.5902	1.449	1.110
	342.07	0.3631	0.6041	1.420	1.121
	341.37	0.4026	0.6260	1.356	1.161
	340.83	0.4339	0.6448	1.317	1.190
	340.40	0.4635	0.6608	1.280	1.220
	339.95	0.4942	0.6782	1.250	1.251
	339.53	0.5247	0.6937	1.220	1.289
	339.17	0.5591	0.7109	1.186	1.331
	338.83	0.5907	0.7269	1.160	1.374
	338.48	0.6246	0.7443	1.136	1.423
	338.19	0.6561	0.7600	1.114	1.475
	337.90	0.6918	0.7785	1.092	1.538
	337.64	0.7265	0.7969	1.073	1.606
	337.39	0.7604	0.8157	1.058	1.681
	337.16	0.7974	0.8373	1.043	1.772
	336.98	0.8340	0.8610	1.031	1.862
	336.86	0.8638	0.8812	1.023	1.949
	336.77	0.8878	0.8989	1.018	2.021
	336.72	0.9098	0.9164	1.015	2.083
	336.70	0.9293	0.9326	1.012	2.144
	336.69	0.9480	0.9490	1.009	2.207
	336.68	0.9655	0.9655	1.009	2.251
	336.71	0.9840	0.9835	1.007	2.318
	x_1Methyl Acetate + x_2Propan-1-ol				
114.66	371.85	0.0108	0.0627	1.948	0.997
	368.13	0.0452	0.2102	1.712	0.998
	363.24	0.0955	0.3746	1.638	1.003
	361.25	0.1172	0.4320	1.622	1.008
	360.49	0.1294	0.4557	1.582	1.009
	357.74	0.1650	0.5287	1.550	1.015
	355.27	0.2023	0.5870	1.502	1.029
	354.53	0.2159	0.6048	1.481	1.032
	352.90	0.2433	0.6396	1.454	1.043
	349.34	0.3177	0.7122	1.373	1.073
	348.19	0.3464	0.7333	1.341	1.090
	346.20	0.4055	0.7702	1.275	1.125
	345.56	0.4253	0.7827	1.259	1.132
	344.24	0.4714	0.8036	1.213	1.178
	343.50	0.4973	0.8151	1.193	1.205
	342.58	0.5328	0.8296	1.165	1.245
	341.87	0.5609	0.8413	1.147	1.274
	341.17	0.5930	0.8527	1.123	1.316
	340.39	0.6276	0.8648	1.103	1.368
	339.77	0.6528	0.8762	1.095	1.382
	339.05	0.6834	0.8872	1.083	1.427
	338.34	0.7175	0.8986	1.068	1.485
	337.57	0.7678	0.9122	1.038	1.622
	337.03	0.7975	0.9213	1.027	1.709
	336.80	0.8066	0.9252	1.027	1.719
	336.47	0.8231	0.9318	1.024	1.740
	336.11	0.8465	0.9388	1.015	1.831
	335.95	0.8616	0.9435	1.007	1.889
	335.38	0.8877	0.9537	1.006	1.959
	335.12	0.9065	0.9604	1.001	2.038
	334.80	0.9204	0.9663	1.002	2.068
	334.42	0.9409	0.9744	1.000	2.154
	334.13	0.9584	0.9815	0.999	2.243
	333.88	0.9732	0.9877	0.998	2.342
	333.69	0.9852	0.9931	0.997	2.401
127.99	0.0096	0.0485	0.0485	1.734	0.994
	372.01	0.0389	0.1781	1.702	0.994
	369.60	0.0633	0.2638	1.644	0.997
	366.94	0.0904	0.3523	1.645	0.997
	364.73	0.1175	0.4181	1.589	1.003
	362.82	0.1415	0.4741	1.573	1.002
	360.79	0.1698	0.5260	1.534	1.011
	359.13	0.1963	0.5658	1.493	1.021
	357.81	0.2198	0.5976	1.459	1.027
	354.65	0.2788	0.6629	1.392	1.057
	353.90	0.2950	0.6785	1.375	1.063
	353.36	0.3069	0.6900	1.365	1.066
	351.63	0.3484	0.7250	1.326	1.081
	350.64	0.3738	0.7426	1.302	1.097

Table 3. continued

p/kPa	T/K	x_1	y_1	γ_1	γ_2
	349.92	0.3888	0.7548	1.299	1.104
	348.92	0.4258	0.7730	1.251	1.135
	348.09	0.4524	0.7864	1.227	1.160
	347.23	0.4818	0.8010	1.203	1.185
	346.54	0.5077	0.8125	1.182	1.211
	345.93	0.5312	0.8225	1.164	1.236
	345.06	0.5670	0.8368	1.139	1.278
	344.30	0.6015	0.8493	1.114	1.326
	343.59	0.6337	0.8620	1.097	1.363
	342.83	0.6709	0.8754	1.076	1.417
	341.99	0.7114	0.8897	1.058	1.485
	341.46	0.7381	0.8990	1.048	1.534
	340.72	0.7752	0.9119	1.035	1.612
	340.07	0.8149	0.9244	1.018	1.730
	339.44	0.8466	0.9374	1.013	1.779
	338.78	0.8846	0.9516	1.005	1.885
	338.25	0.9145	0.9630	1.000	1.993
	337.81	0.9388	0.9728	0.998	2.089
	337.39	0.9619	0.9825	0.997	2.201
	337.03	0.9840	0.9922	0.995	2.376

Table 4. Values of parameters for Eq. (4) and standard deviations in each system

	$Q=g^E/RT$ vs. x_1				
p/kPa	A_0	A_1	A_2	k	$s(g^E/RT)$
	x_1Methyl Acetate$+x_2$Ethanol				
114.66	0.9655	−0.2013	0.2642	1.000	0.0024
127.99	0.5834	0.3542	—	0.138	0.0022
	x_1Methyl Acetate$+x_2$Propan-1-ol				
114.66	0.5534	0.2758	—	0.574	0.0016
127.99	0.4058	0.4058	—	0.205	0.0015

	$Q=(y_1-x_1)$ vs. x_1					
p/kPa	A_0	A_1	A_2	A_3	k	$s(y_1-x_1)$
	x_1Methyl Acetate$+x_2$Ethanol					
114.66	3.281	−6.964	6.750	−3.112	0.526	0.0011
127.99	2.957	−6.749	6.779	−3.059	0.720	0.0012
	x_1Methyl Acetate$+x_2$Propan-1-ol					
114.66	5.055	−4.613	3.542	−3.412	0.108	0.0015
127.99	4.260	−7.079	5.051	−1.697	0.462	0.0015

Table 5. Average errors calculated in the prediction of VLE using different models

System	ASOG, ref. (8)	UNIFAC, ref. (2)			UNIFAC, ref. (9)
	OH/COO	COH/COO	OH/COOC	CCOH/COOC	OH/COOC
		$p=114.66$ kPa (860 Torr)			
Methyl Acetate/Ethanol					
$\bar{e}(\gamma_1)$, %	7.1	1.9	2.4	4.2	14.9
$\bar{e}(y_1)$, %	1.6	1.6	2.2	0.6	5.3
Methyl Acetate/Propan-1-ol					
$\bar{e}(\gamma_i)$, %	6.0	8.6	8.6	7.7	25.2
$\bar{e}(y_1)$, %	2.7	6.1	6.7	5.5	4.8
		$p=127.99$ kPa (960 Torr)			
Methyl Acetate/Ethnaol					
$\bar{e}(\gamma_i)$, %	5.6	1.2	2.0	2.7	11.9
$\bar{e}(y_1)$, %	2.1	1.6	2.4	0.6	5.3
Methyl Acetate/Propan-1-ol					
$\bar{e}(\gamma_i)$, %	3.8	8.5	8.4	7.0	19.7
$\bar{e}(y_1)$, %	3.8	8.1	8.8	7.6	5.6

together with the standard deviation of each fit. The experimental concentration data were also correlated, setting $Q=y_1-x_1$, and the coefficients obtained in each case appear in Table 4 as well. **Figure 1** presents a plot of (y_1-x_1) on x_1, together with the experimental data points. The azeotrope for the methyl acetate/ethanol system was calculated from the correlation of the experimental data and by interpolation. At 114.66 kPa there was an azeotrope at $x_1=0.954$ and $T=333.4$ K, and at 127.99 kPa the azeotrope formed at $x_1=0.948$ and $T=336.7$ K.

Using the same fitting coefficients values for g^E/RT on x_1, the activity coefficients were represented indirectly, using the corresponding thermodynamic relations for determining γ_1 from $Q=g^E/RT$ and Q'.

Generalizing the degree of Eq. (4), the activity coefficients for the two components were:

$$\ln\gamma_1=x_2^2\left[\sum_{i=0}^{m}A_iZ^i+x_1k(Z/x_1)^2\sum_{i=1}^{m-1}iA_iZ^{i-1}\right] \quad (5)$$

$$\ln\gamma_2=x_1^2\left[\sum_{i=0}^{m}A_iZ^i-x_2k(Z/x_1)^2\sum_{i=1}^{m-1}iA_iZ^{i-1}\right] \quad (6)$$

where "Z" is related to the composition, x_1, by the expression in brackets of Eq. (4): $Z=x_1/(x_1+kx_2)$.

3. Predicting Isobaric VLE Values Using Group-Contribution Models

As in the previous papers in this series, the isobaric equilibrium data were predicted using the UNIFAC

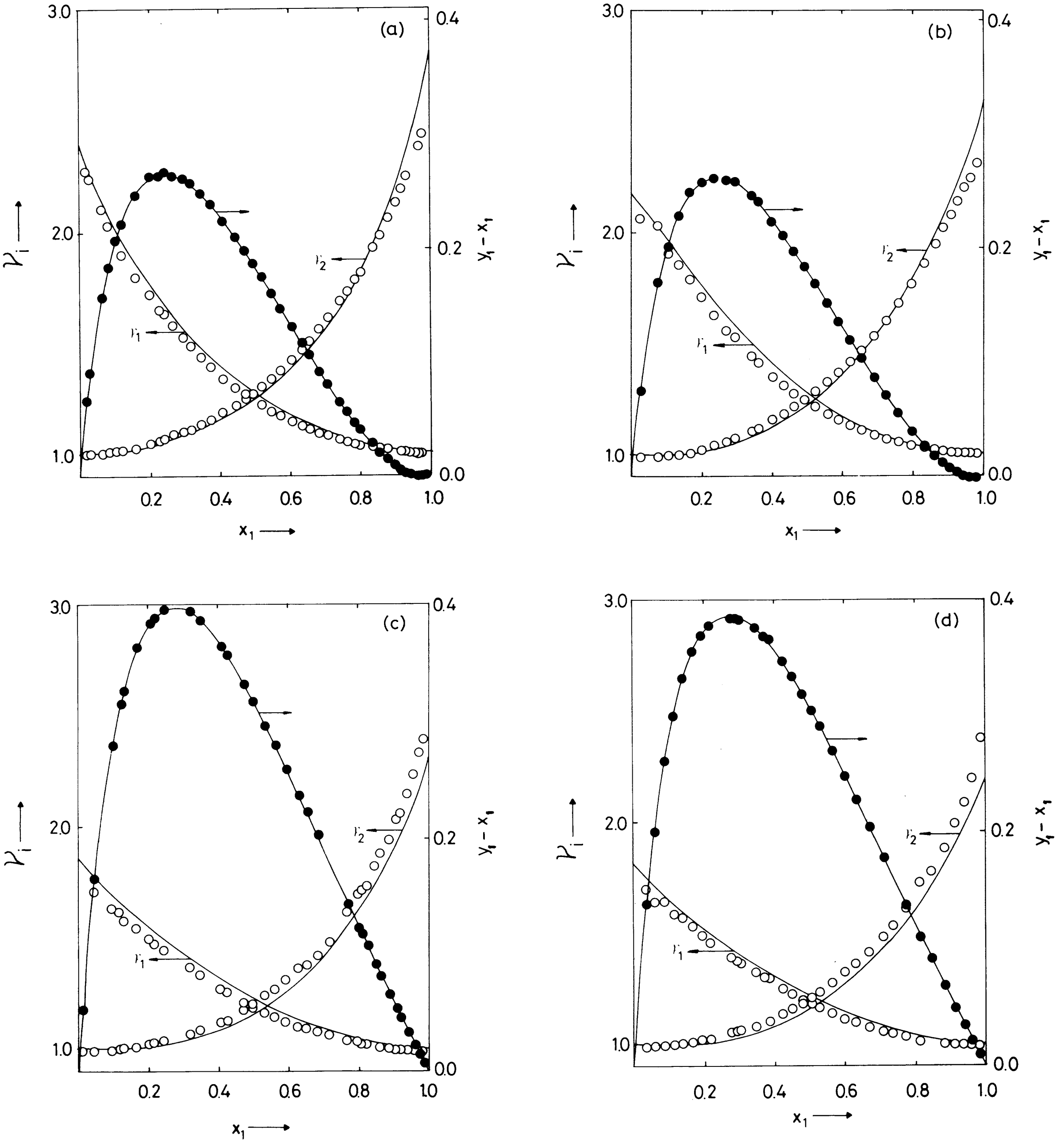

Fig. 1. Plot of $(y_1 - x_1)$ and γ_i versus x_1 for $x_1$methyl acetate+$x_2$ethanol at 114.66 kPa (a) and at 127.99 kPa (b), and for $x_1$methyl acetate+$x_2$propan-1-ol at 114.66 kPa (c) and at 127.99 kPa (d). ●, ○: experimental values of $(y_1 - x_1)$ and γ_i, —, fitting curves.

model by Fredenslund *et al.*[3] and the ASOG model by Kojima and Tochigi.[8] In the present study, an additional version of the UNIFAC model, that given by Larsen *et al.*,[9] was also used to perform the pediction, in order to expand the application of these predictive models. All the predictions were evaluated by comparing the activity coefficients, γ_i, and the concentrations of the vapor phase, y_1, obtained from (p, x_i) values. The mean errors for each of the variables discussed above are set out for each system in **Table 5**. A single case was considered for the ASOG and modified UNIFAC models respectively, i.e., the interaction pair OH/COO for the ASOG model[8] and OH/COOC for the modified UNIFAC model.[9] However, in the case of the conventional UNIFAC model all three cases of interaction groups contained in the literature were considered, i.e., COH/COO,[2] OH/COOC[16] and CCOH/COOC.[1] The results of the version of the UNIFAC model developed by Larsen *et al.*[9] were rejected, because of the high mean errors of around 18% produced in predicting the activity coefficients. On the other hand, the estimates obtained using the ASOG model and the three cases of the conventional UNIFAC model yielded the resuls expected, i.e., mean errors of around 5%, with slightly better results at the higher pressure.

The azeotropes predicted by the various models for the methyl acetate/ethanol system were as follows. At a pressure of 114.66 kPa, the ASOG model and the three cases of the conventional UNIFAC model gave similar values, around $x_1=0.925$; the modified UNIFAC model gave $x_1=0.870$, considerably different from the experimental value of 0.954. At a pressure of 127.99 kPa, the ASOG model and the conventional UNIFAC model predicted a singular point at $x_1=0.929$, whereas the modified UNIFAC model yielded $x_1=0.866$, as opposed to an experimental value of 0.948.

The lower precision of the modified UNIFAC model can be explained by the fact that, as the number of properties (VLE, h^E, etc.) predicted by a model increases, its ability to represent or reproduce a particular property decreases.

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Nomenclature

A, B, C = constants of Antoine equation [—]
A_i = parametrs of Eq. (4) [—]
B_{ij} = cross second virial coefficient [$\mathrm{m^3 \cdot mol^{-1}}$]
g^E = excess free energy [$\mathrm{J \cdot mol^{-1}}$]
k = parametr of Eq. (4) [—]
p_i° = vapor pressure of component i [kPa]
p = total pressure [kPa]
R = universal gas constant [$\mathrm{J \cdot K^{-1} mol^{-1}}$]
s = standard deviation [—]
T = temperature [K]
v_i^L = molar volume of component i [$\mathrm{m^3 mol^{-1}}$]
x = liquid-phase mole fraction [—]
y = vapor-phase mole fraction [—]
$\bar{e}(z)$ = mean error of z [%]

γ_i = activity coefficient of component i [—]
ϕ_i = fugacity coefficient of component i [—]

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