Vapor−Liquid Equilibria and Densities for Ethyl Esters (Ethanoate to Butanoate) and Alkan-2-ol (C_3−C_4) at 101.32 kPa

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Vapor−liquid equilibrium at 101.32 kPa has been measured for the binary systems formed by ethyl ethanoate, propanoate, and butanoate with propan-2-ol and butan-2-ol in an equilibrium still with circulation of both the vapor and liquid phases. The data were correlated by several available equations, and the parameters are reported for each of mixtures studied. Azeotropes were found in the mixtures ethyl ethanoate or propanoate + propan-2-ol and ethyl propanoate + butan-2-ol. Satisfactory results are obtained for the prediction of activity coefficients and the equilibrium compositions with the UNIFAC modified model. The densities for the same mixtures at 298.15 K are also reported.

Introduction

As an extension of our earlier work concerning vapor−liquid equilibria (VLE) for mixtures of alkyl esters and alkanols underway at our laboratory, this paper presents VLE results for mixtures of ethyl ethanoate, propanoate, and butanoate with propan-2-ol and butan-2-ol at a pressure of 101.32 kPa. The literature contains isobaric and isothermal VLE measurements for the system ethyl ethanoate + propan-2-ol. However, a redetermination was necessary in view of the discrepancies in the isobaric VLE values reported in the literature. The results are compared with ASOG model of Tochigi et al. (1990) and the original version of UNIFAC published by Fredenslund et al. (1975) and the UNIFAC version as modified by Gmehling et al. (1993).

Experimental Section

Materials. The chemicals used in the experiment were the highest commercial grade from Fluka. Before use they were degassed using ultrasound and dried on a molecular sieve (0.3 nm from Fluka). Table 1 gives the physical properties of the alkan-2-ols and the ethyl esters as determined experimentally at atmospheric pressure. Comparison with literature values yielded good agreement.

Equipment and Procedure. VLE measurements were made in a small-capacity (around 60 cm^3) equilibrium still in which both phases were refluxed. The ebulliometer and auxiliary pressure and temperature systems have been described previously by Ortega and Susial (1991). Phase concentrations were obtained by densimetry, using an Anton Paar model DMA-55 densimeter with a precision of ± 0.02 $k\cdot gm^{-3}$ controlled to (298.15 ± 0.01) K and calibrated with bidistilled and degassed water and nonane, according to Ortega et al. (1985). Densimetry was used to establish standard curves for each of the ethyl ester (1) + alkan-2-ol (2) binary systems after the density−composition curves for the ester had been plotted. Good correlations can be achieved using simple polynomial expressions of the type $\rho = \sum a_i x_1^i$ and can in turn be used to determine the concentrations for each of the equilibrium states. Precision of the ester mole fraction values for the both the liquid and the vapor phases was better than ±0.002 units.

Results and Discussion

Densities and Excess Volumes. The excess volume, V_m^E, values were also determined to validate the quality of the density value measurements for each standard mixture. The V_m^E values were obtained using the density values for the pure components and for the ethyl ester (1) + alkan-2-ol (2) binary mixtures at (298.15 ± 0.01) K listed in Table 2. The value pairs (x_1, V_m^E) were fitted using the following polynomial equation:

$$10^9 V_m^E/(m^3\cdot mol^{-1}) = z_1 z_2 \sum A_i z_1^i \quad \text{where} \quad z_1 = x_1/(x_1 + k_v x_2) \quad \text{and} \quad z_2 = 1 - z_1 \qquad (1)$$

Table 3 presents the values for the parameters A_i and k_v calculated by correlating the excess volume data using a least-squares method. The degree of the polynomial was optimized in each case using an *F*-test at a constant value of the parameter k_v, the quotient of the molar volumes of the pure components, V_2/V_1, for each mixture at the same working temperature (Ortega and Alcalde, 1992). The experimental values are compared with the correlations in Figure 1a,b. There was good agreement between the experimental results for ethyl ethanoate (1) + propan-2-ol (2) and the values published by Grolier and Viallard (1971), with differences of less than 2%; on the other hand, the estimated discrepancy with respect to the values published by Nikam et al. (1996), which are skewed with respect to the two other curves, was 11%. All the binary systems exhibited volumetric expansion effects, with the V_m^E values increasing with alkan-2-ol chain length, which accounts for the steric hindrance of the molecules. The insets in Figure 1a,b graphically compare the equimolar values for this excess magnitude for the *sec*-alkanols and different alkyl esters. The easiest interpretation is to attribute the decrease in the V_m^E values for these mixtures with alkyl ester chain length to improve coupling between the alkanol and ester molecules as a result of greater flexibility of the ester chain around the −COO− group as the number of CH_2 groups increases. However, the insets in Figure 1a,b show that the decrease in the values with ester chain length was not uniform, in part because of ester−alkanol complexation. This feature is even more pronounced in the case of methanoates, although the explanation requires an analysis of additional mixing properties that falls outside the scope of the present paper.

Pure Component Vapor Pressures. Accordingly, Table 4 gives the vapor pressures for the three ethyl esters, determined using the same VLE equipment described

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Table 1. Physical Properties Measured for Pure Compounds Used in This Work and Literature Values for Comparison

	$T^\circ_{b,1}$/K		ρ(298.15 K)/(kg·m^{-3})		n(D, 298.15 K)		ω	
compound	exptl	lit.	exptl	lit.	exptl	lit.	calcd	lit.
ethyl ethanoate	350.25	350.26[a]	894.34	894.55[a] 894.53[b]	1.3699	1.36979[c] 1.36978[a]	0.362	0.362[d]
ethyl propanoate	371.92	372.16[c] 372.25[a]	883.93	884.00[a,c]	1.3811	1.3814[a,c]	0.392	0.391[d]
ethyl butanoate	394.18	394.65[c] 394.70[a]	873.94	873.70[c] 873.94[a]	1.3898	1.3900[c]	0.421	0.461[d]
propan-2-ol	355.39	355.39[a] 355.48[c]	780.77	781.26[a] 780.82[c]	1.3752	1.3752[a] 1.3753[ac]	0.668	0.665[d]
butan-2-ol	372.39	372.65[c] 372.66[a]	802.34	802.41[a] 802.30[ac]	1.3949	1.3953[a] 1.3949[c]	0.568	0.577[d]

[a] Riddick et al. (1986). [b] Grolier and Viallard (1971). [c] TRC (1990). [d] Reid et al. (1977).

Table 2. Densities and Excess Volumes at 298.15 K of Ethyl Esters (1) + Propan-2-ol (2) or Butan-2-ol (2)

x_1	ρ/(kg·m^{-3})	$10^9V^E_m$/(m^3·mol^{-1})	x_1	ρ/(kg·m^{-3})	$10^9V^E_m$/(m^3·mol^{-1})	x_1	ρ/(kg·m^{-3})	$10^9V^E_m$/(m^3·mol^{-1})
			$CH_3COOC_2H_5$ (1)+$CH_3CH(OH)CH_3$ (2)					
0.0000	780.77	0	0.2974	816.63	410	0.6423	855.60	452
0.0381	785.44	78	0.3484	822.62	436	0.6887	860.71	420
0.0860	791.36	158	0.3910	827.47	463	0.7500	867.39	368
0.1257	796.14	225	0.4446	833.56	482	0.8143	874.24	309
0.1690	801.34	288	0.4871	838.40	484	0.8609	879.33	241
0.2113	806.46	331	0.5368	844.02	476	0.9255	886.25	143
0.2522	811.36	368	0.5945	850.40	466	1.0000	894.34	0
			$CH_3COOC_2H_5$ (1) + $CH_3CH_2CH(OH)CH_3$ (2)					
0.0000	802.34	0	0.3264	828.62	568	0.6729	860.62	547
0.0617	806.77	172	0.3784	833.20	601	0.7273	865.90	501
0.0888	808.96	223	0.4120	836.15	621	0.7809	871.26	434
0.1354	812.62	320	0.4745	841.82	634	0.8286	876.14	360
0.2003	817.91	428	0.5228	846.25	633	0.8757	880.95	285
0.2222	819.72	460	0.5730	850.92	623	0.9257	886.30	176
0.2671	823.52	512	0.6254	855.99	587	1.0000	894.34	0
			$C_2H_5COOC_2H_5$ (1) + $CH_3CH(OH)CH_3$ (2)					
0.0000	780.77	0	0.2649	814.30	283	0.6057	849.57	365
0.0386	786.06	56	0.3079	819.08	321	0.6775	856.07	355
0.0709	790.39	98	0.3486	823.63	335	0.7197	859.85	335
0.1094	795.36	148	0.4039	829.50	361	0.7809	865.29	286
0.1485	800.23	199	0.4427	833.58	366	0.8533	871.55	213
0.1808	804.32	219	0.4988	839.23	376	0.9396	878.84	98
0.2275	809.86	266	0.5554	844.72	381	1.0000	883.93	0
			$C_2H_5COOC_2H_5$ (1) + $CH_3CH_2CH(OH)CH_3$ (2)					
0.0000	802.34	0	0.2956	826.71	437	0.6451	855.15	479
0.0532	806.63	112	0.3413	830.48	468	0.6953	859.21	444
0.0970	810.24	194	0.3983	835.19	492	0.7545	863.97	393
0.1320	813.22	243	0.4351	838.13	512	0.8072	868.20	336
0.1719	816.45	309	0.4896	842.54	523	0.8657	872.92	256
0.2120	819.86	348	0.5406	846.70	517	0.9234	877.68	152
0.2520	823.03	408	0.5931	850.95	504	1.0000	883.93	0
			$C_3H_7COOC_2H_5$ (1) + $CH_3CH(OH)CH_3$ (2)					
0.0000	780.77	0	0.2861	816.45	278	0.6676	850.62	333
0.0356	785.85	54	0.3435	822.38	308	0.7747	858.48	286
0.0857	792.72	110	0.4033	828.17	336	0.8435	863.42	213
0.1306	798.49	158	0.4593	833.31	354	0.9286	869.15	122
0.1853	805.20	203	0.5257	839.12	363	1.0000	873.94	0
0.2415	811.60	250	0.5973	845.07	355			
			$C_3H_7COOC_2H_5$ (1) + $CH_3CH_2CH(OH)CH_3$ (2)					
0.0000	802.34	0	0.3209	827.36	448	0.6690	851.61	445
0.0364	805.33	75	0.3637	830.48	474	0.7243	855.22	405
0.0796	808.80	159	0.4150	834.17	494	0.7888	859.40	340
0.1174	811.81	222	0.4567	837.18	496	0.8503	863.31	266
0.1578	814.98	283	0.5061	840.56	508	0.9106	867.14	172
0.1962	817.99	329	0.5649	844.69	486	0.9177	867.62	155
0.2327	820.76	373	0.6186	848.34	462	1.0000	873.94	0
0.2761	824.02	416						

Table 3. Constants of Eq 1 Obtained in Correlation of Excess Volumes, $k_v = V_2/V_1$

compound	10^6V_i/(m^3·mol^{-1})	k_v	A_0	A_1	A_2	10^9 s(V^E_m)/m^3·mol^{-1})
ethyl ethanoate (1) +	98.52					
propan-2-ol (2)	76.97	0.781	1714	−175	1103	4
butan-2-ol (2)	92.38	0.938	2708	−801	890	4
ethyl propanoate (1) +	115.54					
propan-2-ol (2)	76.97	0.666	1177	−428	1858	6
butan-2-ol (2)	92.38	0.799	1842	−88	1008	4
ethyl butanoate (1) +	132.92					
propan-2-ol (2)	76.97	0.579	1021	−773	2566	6
butan-2-ol (2)	92.38	0.695	1639	−15	1296	6

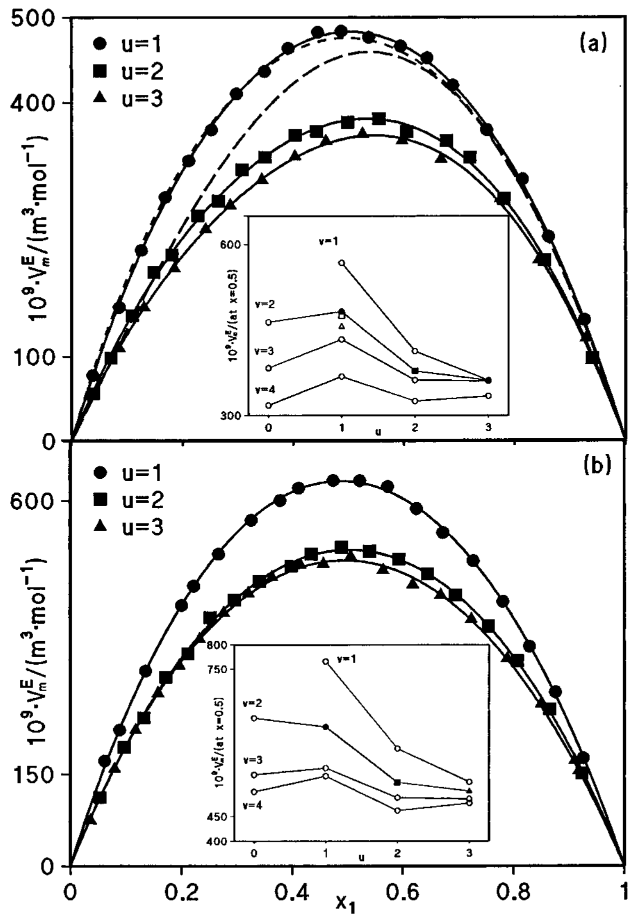

Figure 1. Representations of experimental values and curves of V_m^E for $C_uH_{2u+1}CO_2C_2H_5$ (1) + alkan-2-ol (2): (a) + propan-2-ol (- - -), Grolier and Viallard (1971); (— — —) Nikam et al. (1996); (b) + butan-2-ol. Insets correspond to the comparison between equimolar V_m^E values of different alkyl esters, $C_uH_{2u+1}CO_2C_vH_{2v+1}$, with propan-2-ol in (a) [□, Grolier and Viallard (1971); △, Nikam et al. (1996)] and with butan-2-ol in (b).

Table 4. Experimental Values of Vapor Pressures, $p°$, and Temperature, T, for Ethyl Ethanoate, Ethyl Propanoate, and Ethyl Butanoate

T/K	$p°$/kPa	T/K	$p°$/kPa	T/K	$p°$/kPa
		Ethyl Ethanoate			
364.88	160.97	350.25	101.32	342.49	78.40
364.36	158.40	350.09	101.15	341.97	77.00
364.27	157.93	349.68	99.81	341.48	75.75
363.78	155.59	349.30	98.59	340.98	74.43
363.21	152.87	348.76	96.86	340.41	72.97
362.48	149.53	348.47	95.93	340.10	72.18
361.77	146.28	347.99	94.39	339.43	70.48
361.09	143.28	347.59	93.17	338.82	69.02
360.63	141.31	347.15	91.87	338.32	67.80
359.48	136.27	346.74	90.55	337.77	66.49
358.83	133.54	346.31	89.29	337.09	64.89
357.03	126.28	345.81	87.80	336.06	62.52
356.34	123.56	345.39	86.53	334.52	59.15
355.64	120.84	344.92	85.17	333.37	56.68
354.46	116.48	344.46	83.90	331.79	53.31
352.93	110.85	343.91	82.33	330.13	50.28
351.05	104.36	343.49	81.15		
350.22	101.57	342.92	79.59		
		Ethyl Propanoate			
388.29	163.42	375.89	114.04	368.29	90.29
387.57	160.18	375.45	112.62	367.81	89.04
386.84	156.78	375.14	111.47	367.36	87.77
385.99	152.99	374.70	110.09	366.86	86.35
385.33	150.16	374.31	108.73	366.38	85.01
384.50	146.66	373.86	107.30	365.87	83.72
383.69	143.28	373.44	106.01	365.37	82.34
382.68	139.18	373.09	104.87	364.86	81.02
382.02	136.48	372.74	103.81	364.33	79.66
381.09	132.90	372.18	102.00	363.86	78.46
380.26	129.71	372.10	101.69	363.37	77.20
379.42	126.59	371.92	101.32	362.34	74.66
378.92	124.85	371.94	101.15	361.70	73.11
378.57	123.48	371.51	99.78	360.32	69.87
378.18	122.09	371.02	98.39	358.90	66.65
377.82	120.74	370.60	97.03	357.36	63.28
377.47	119.51	370.13	95.65	355.84	60.08
377.08	118.21	369.70	94.39	354.08	56.54
376.75	116.99	369.21	93.01	352.23	53.00
376.30	115.50	368.79	91.79	350.57	50.01
		Ethyl Butanoate			
407.37	146.79	398.50	114.65	389.30	87.74
406.68	144.01	398.17	113.66	388.37	85.14
405.93	141.19	396.92	109.54	387.41	82.81
405.28	138.77	395.78	106.05	386.23	79.85
404.53	135.96	395.22	104.32	385.21	77.36
403.76	133.05	394.18	101.32	384.06	74.74
403.20	130.94	394.18	101.28	382.79	71.84
402.62	128.97	394.16	101.22	381.71	69.43
401.73	125.76	393.53	99.37	380.48	66.77
400.95	122.98	392.73	97.13	379.14	63.96
400.17	120.35	392.05	95.16	377.86	61.31
399.41	117.80	391.37	93.27	376.40	58.54
399.22	116.98	390.40	90.70	374.94	55.78

above. The values were correlated by means of the Antoine equation using a nonlinear regression procedure, and the values of the constants A, B, and C are given in Table 5 together with the values published earlier for the alkan-2-ols. The largest discrepancies, deviations of around 2%, were observed for ethyl butanoate.

The value pairs (T, $p°$) were correlated linearly using the reduced coordinate set, and the regression line is plotted in Figure 2 along with those of other compounds used in this work. The acentric factors, ω, for the components for the same working temperature range were calculated and are listed in Table 1 for use in the computations for the VLE values. Once again, the largest discrepancies were recorded for ethyl butanoate.

VLE Values and Correlations. Table 6 presents the experimental isobaric VLE values for the binary mixtures consisting of ethyl ester (1) + alkan-2-ol (2) at (101.32 ± 0.05) kPa. The activity coefficient, γ_i, values were calculated on the assumption that the vapor phase was nonideal using the equation

$$\gamma_i = [\phi_i p y_i/(p° x_i \phi_i^\circ)] \exp[(p° - p)V_i^\circ/RT] \qquad (2)$$

where the fugacity coefficients, ϕ_i and ϕ_i°, were calculated using

$$\phi_i = \exp[(2\sum_k y_k B_{ik} - \sum_j \sum_k y_j y_k B_{jk})p/RT] \qquad (3)$$

To calculate the molar volumes, V_i°, as a function of temperature for the pure components using eq 2, a modified version of Rackett's equation was used to determine Rackett's parameters, Z_{RA}, not found in literature by an empirical expression [see Reid et al. (1977)], from the acentric factors presented in Table 1. The values of the virial coefficients for pure compounds and mixtures in eq 3 were calculated using the correlations published by Tsonopoulos (1974). The vapor pressures, $p°$, were calculated at each equilibrium temperature using the Antoine equation and the constant values from Table 5. The influence of the different sets of constant values from Table 5 on the calculations of the activity coefficient values was reflected in the mean differences, less than 0.5% for the mixtures containing ethyl ethanoate and 4% for the mixtures containing ethyl butanoate. Application of the point-to-point test of Fredenslund et al. (1977) yielded a mean deviation for the set of points for each system, δy_i,

Table 5. Antoine Equation[a] Constants, *A*, *B*, and *C*, along with Values from Literature for Pure Substances Used in This Work

compound	*A*	*B*	*C*	range of *T*/K	*s*(*p*°)	% mean error	references
ethyl ethanoate	6.572 59	1465.78	−29.18	300−390			this work
	6.133 61	1195.13	−60.68	259−372		0.4	TRC (1990)
	6.187 99	1224.67	−57.44	271−372		0.6	Riddick et al. (1986)
	6.139 45	1211.90	−57.15	260−385		0.6	Reid et al. (1977)
	6.226 69	1244.95	−55.27	288−348		0.4	Boublik et al. (1973)
ethyl propanoate	6.334 31	1404.22	−47.58	315−420	0.07		this work
	6.144 00	1274.70	−64.15	278−398		0.8	TRC (1990)
	6.134 87	1268.94	−64.85			0.8	Riddick et al. (1986)
	6.143 97	1274.70	−64.16	276−396		0.8	Reid et al. (1977)
	6.119 82	1260.62	−65.75	306−371		0.8	Boublik et al. (1973)
ethyl butanoate	6.360 31	1493.89	−51.13	330−435	0.06		this work
	5.274 56	921.56	−112.77	298−423		2.1	TRC (1990)
	6.073 05	1358.30	−60.15	288−432		1.3	Reid et al. (1977)
propan-2-ol	7.111 50	1505.94	−60.15	300−400			Ortega and Susial (1991)
butan-2-ol	6.312 86	1159.84	−102.90	310−420			Ortega and Hernández (1996)

[a] $\log(p°/\mathrm{kPa}) = A - B/(T/\mathrm{K} + C)$.

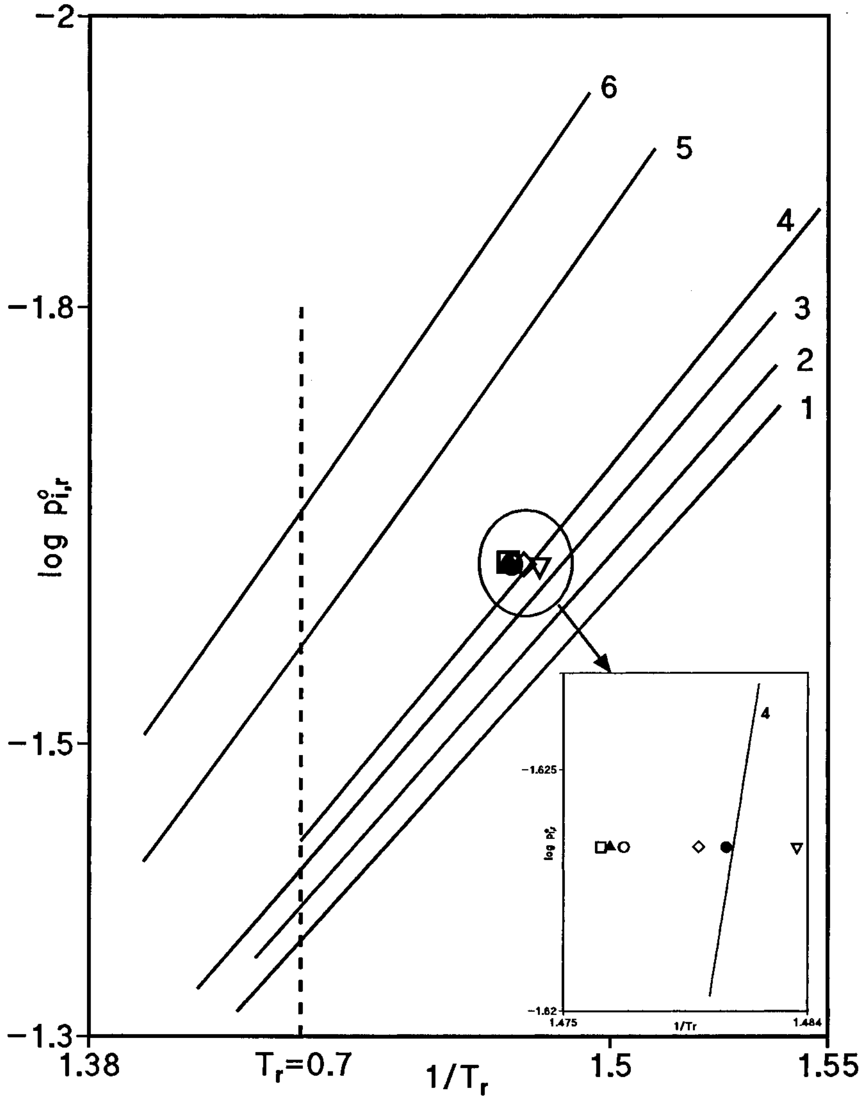

Figure 2. Reduced vapor pressure lines using the Antoine equation and coefficients from Table 5 for the pure compounds: 1, ethyl ethanoate; 2, ethyl propanoate; 3, ethyl butanoate; 4, azeotropic line for ethyl ethanoate + propan-2-ol; 5, propan-2-ol; 6, butan-2-ol. Inset shows the comparison between the azeotropic points from the literature and ours for ethyl ethanoate (1) + propan-2-ol (2). ●, our experimental azeotrope; ▲, Murti and van Winkle (1958); □, Nishi (1972); ○, Rajendran et el. (1991) [◆, Lecat (1926) and ▽, Durrans (1920); see Gmehling et al. (1994)].

of less than 0.01 and a positive consistency according to that method.

The treatment of the VLE values presented in Table 6 was performed using the software put forward by Prausnitz et al. (1980) based on the principle of maximun likelihood applied to equations commonly used to process the VLE values. However, that same software was also used with other polynomial equations, such as the Redlich−Kister equation and another equation similar to eq 1 in which the values of *k* were optimized. Table 7 gives the results achieved by applying the different correlations to the values from Table 6, together with the mean deviations obtained

Table 6. Experimental VLE Values at 101.32 kPa for the Mixtures Ethyl Alkanoates (C_2−C_4) (1) + Propan-2-ol (2) or Butan-2-ol (2)

T/K	x_1	y_1	γ_1	γ_2	G^E/RT	T/K	x_1	y_1	γ_1	γ_2	G^E/RT	T/K	x_1	y_1	γ_1	γ_2	G^E/RT
$CH_3COOC_2H_5$ (1) + $CH_3CH(OH)CH_3$ (2)																	
355.39	0.000	0.000		1.000	0.000	349.58	0.339	0.440	1.322	1.051	0.128	348.11	0.724	0.720	1.060	1.335	0.122
354.71	0.029	0.053	1.600	0.990	0.004	349.29	0.370	0.465	1.291	1.066	0.135	348.12	0.726	0.721	1.059	1.338	0.121
354.47	0.038	0.070	1.598	0.991	0.009	349.02	0.401	0.492	1.270	1.077	0.140	348.13	0.730	0.725	1.057	1.343	0.120
354.17	0.051	0.092	1.595	0.992	0.016	348.80	0.437	0.517	1.234	1.098	0.145	348.14	0.733	0.728	1.057	1.342	0.119
353.78	0.067	0.118	1.579	0.994	0.025	348.65	0.464	0.536	1.213	1.113	0.147	348.14	0.747	0.738	1.053	1.360	0.116
353.47	0.081	0.141	1.574	0.995	0.032	348.50	0.489	0.553	1.192	1.132	0.149	348.19	0.766	0.754	1.047	1.380	0.111
353.15	0.097	0.165	1.562	0.996	0.040	348.37	0.516	0.572	1.172	1.152	0.150	348.28	0.789	0.774	1.039	1.404	0.102
352.69	0.117	0.196	1.543	1.000	0.051	348.23	0.555	0.599	1.146	1.181	0.150	348.39	0.816	0.798	1.033	1.434	0.093
352.37	0.134	0.220	1.533	1.001	0.058	348.14	0.592	0.621	1.117	1.222	0.147	348.51	0.843	0.822	1.026	1.471	0.082
352.05	0.152	0.244	1.516	1.003	0.066	348.12	0.605	0.631	1.111	1.229	0.145	348.66	0.868	0.846	1.021	1.501	0.072
351.71	0.171	0.268	1.493	1.007	0.074	348.11	0.620	0.642	1.105	1.238	0.143	348.86	0.897	0.875	1.016	1.543	0.059
351.37	0.194	0.297	1.472	1.009	0.082	348.10	0.636	0.653	1.097	1.252	0.141	349.02	0.915	0.895	1.013	1.565	0.050
350.99	0.222	0.327	1.437	1.015	0.092	348.10	0.657	0.670	1.088	1.267	0.137	349.27	0.934	0.917	1.009	1.580	0.039
350.67	0.243	0.351	1.423	1.018	0.099	348.09	0.680	0.687	1.079	1.285	0.132	349.49	0.958	0.943	1.005	1.666	0.026
350.39	0.264	0.371	1.397	1.026	0.107	348.10	0.698	0.702	1.071	1.303	0.128	349.86	0.984	0.978	1.003	1.649	0.011
350.12	0.286	0.391	1.371	1.035	0.115	348.09	0.711	0.711	1.067	1.317	0.126	350.25	1.000	1.000	1.000		0.000
349.85	0.310	0.416	1.357	1.038	0.120	348.10	0.723	0.719	1.061	1.333	0.122						
$CH_3COOC_2H_5$ (1) + $CH_3CH_2CH(OH)CH_3$ (2)																	
372.39	0.000	0.000		1.000	0.000	364.08	0.220	0.420	1.266	0.998	0.050	353.96	0.704	0.824	1.041	1.187	0.079
371.75	0.015	0.033	1.213	0.996	-0.001	362.54	0.273	0.485	1.226	1.010	0.063	353.43	0.740	0.848	1.035	1.198	0.072
370.95	0.033	0.077	1.260	0.998	0.006	359.90	0.372	0.592	1.186	1.025	0.079	352.73	0.787	0.874	1.024	1.251	0.066
370.15	0.049	0.120	1.367	0.995	0.011	358.52	0.441	0.649	1.142	1.046	0.084	352.15	0.832	0.902	1.019	1.256	0.054
369.50	0.067	0.156	1.321	0.996	0.015	357.93	0.472	0.672	1.124	1.059	0.085	351.66	0.870	0.923	1.012	1.300	0.044
367.75	0.113	0.249	1.313	0.993	0.025	356.47	0.548	0.729	1.096	1.084	0.087	351.12	0.913	0.949	1.008	1.328	0.032
366.93	0.134	0.289	1.319	0.992	0.030	355.75	0.592	0.757	1.077	1.107	0.085	350.66	0.952	0.972	1.005	1.318	0.018
365.72	0.167	0.344	1.304	0.994	0.039	355.10	0.634	0.780	1.057	1.146	0.085	350.37	0.977	0.987	1.004	1.252	0.009
365.04	0.190	0.373	1.263	1.003	0.047	354.54	0.666	0.801	1.051	1.165	0.084	350.25	1.000	1.000	1.000		0.000
$C_2H_5COOC_2H_5$ (1) + $CH_3CH(OH)CH_3$ (2)																	
355.39	0.000	0.000		1.000	0.000	355.39	0.177	0.160	1.508	1.009	0.080	358.05	0.542	0.398	1.127	1.174	0.138
355.29	0.024	0.027	1.866	0.990	0.005	355.42	0.186	0.167	1.499	1.011	0.084	358.42	0.572	0.420	1.113	1.194	0.137
355.28	0.037	0.039	1.798	0.990	0.012	355.46	0.197	0.175	1.479	1.014	0.088	358.76	0.595	0.436	1.097	1.214	0.134
355.27	0.049	0.052	1.774	0.990	0.019	355.52	0.211	0.185	1.456	1.017	0.093	359.49	0.641	0.475	1.086	1.238	0.130
355.26	0.059	0.062	1.750	0.991	0.025	355.57	0.228	0.197	1.437	1.021	0.099	360.80	0.714	0.541	1.065	1.295	0.119
355.25	0.071	0.073	1.715	0.992	0.031	355.68	0.252	0.213	1.398	1.029	0.106	361.84	0.761	0.588	1.051	1.338	0.107
355.24	0.078	0.079	1.698	0.994	0.036	355.75	0.269	0.224	1.376	1.035	0.111	362.63	0.792	0.625	1.046	1.362	0.100
355.24	0.087	0.087	1.689	0.994	0.040	355.85	0.286	0.236	1.356	1.040	0.115	363.93	0.832	0.677	1.035	1.390	0.084
355.24	0.090	0.090	1.681	0.994	0.041	355.92	0.298	0.244	1.343	1.044	0.118	364.73	0.857	0.711	1.030	1.420	0.075
355.25	0.095	0.095	1.664	0.995	0.044	356.05	0.322	0.258	1.314	1.054	0.124	365.62	0.878	0.742	1.022	1.437	0.063
355.26	0.105	0.102	1.633	0.997	0.049	356.20	0.344	0.273	1.291	1.063	0.128	366.47	0.899	0.778	1.019	1.455	0.055
355.27	0.115	0.111	1.619	0.998	0.054	356.37	0.371	0.290	1.265	1.075	0.133	367.10	0.916	0.807	1.019	1.481	0.050
355.28	0.124	0.118	1.597	1.000	0.058	356.59	0.400	0.307	1.235	1.090	0.136	368.06	0.935	0.845	1.015	1.483	0.040
355.30	0.133	0.126	1.581	1.001	0.062	356.84	0.428	0.326	1.213	1.103	0.139	368.83	0.951	0.878	1.014	1.512	0.033
355.32	0.145	0.135	1.559	1.003	0.067	357.10	0.456	0.344	1.189	1.119	0.140	369.55	0.966	0.911	1.014	1.534	0.028
355.35	0.154	0.143	1.548	1.004	0.071	357.33	0.479	0.358	1.171	1.133	0.141	370.65	0.982	0.951	1.007	1.573	0.015
355.37	0.164	0.150	1.526	1.007	0.075	357.67	0.511	0.380	1.151	1.152	0.141	371.92	1.000	1.000	1.000		0.000
$C_2H_5COOC_2H_5$ (1) + $CH_3CH_2CH(OH)CH_3$ (2)																	
372.39	0.000	0.000		1.000	0.000	369.96	0.308	0.351	1.211	1.015	0.069	369.33	0.632	0.630	1.079	1.113	0.087
372.29	0.015	0.021	1.340	0.991	-0.005	369.76	0.350	0.390	1.193	1.022	0.076	369.40	0.679	0.672	1.068	1.130	0.084
372.18	0.029	0.039	1.331	0.990	-0.001	369.62	0.394	0.431	1.175	1.028	0.080	369.49	0.716	0.705	1.060	1.145	0.080
372.02	0.051	0.066	1.285	0.990	0.003	369.53	0.424	0.459	1.166	1.032	0.083	369.63	0.761	0.747	1.053	1.157	0.074
371.85	0.069	0.090	1.311	0.989	0.008	369.45	0.462	0.490	1.143	1.046	0.086	369.77	0.804	0.787	1.045	1.184	0.068
371.65	0.090	0.116	1.308	0.990	0.015	369.39	0.503	0.523	1.122	1.062	0.088	369.87	0.820	0.804	1.043	1.186	0.065
371.38	0.123	0.154	1.273	0.993	0.024	369.37	0.537	0.550	1.106	1.075	0.088	370.47	0.895	0.882	1.031	1.195	0.046
371.25	0.139	0.172	1.266	0.994	0.028	369.34	0.555	0.565	1.101	1.082	0.088	370.80	0.931	0.921	1.024	1.205	0.035
371.15	0.151	0.186	1.264	0.995	0.031	369.33	0.576	0.583	1.096	1.089	0.089	371.10	0.967	0.963	1.022	1.187	0.027
370.70	0.209	0.249	1.241	1.000	0.045	369.33	0.600	0.605	1.091	1.093	0.088	371.92	1.000	1.000	1.000		0.000
$C_3H_7COOC_2H_5$ (1) + $CH_3CH(OH)CH_3$ (2)																	
355.39	0.000	0.000		1.000	0.000	358.51	0.246	0.117	1.442	1.030	0.112	368.70	0.687	0.336	1.053	1.294	0.116
355.67	0.026	0.014	1.839	0.990	0.006	358.81	0.274	0.128	1.408	1.044	0.125	369.70	0.709	0.353	1.040	1.310	0.106
355.70	0.028	0.015	1.862	0.990	0.008	359.41	0.313	0.145	1.371	1.057	0.137	370.70	0.732	0.376	1.038	1.325	0.103
355.92	0.048	0.025	1.749	0.992	0.019	360.10	0.353	0.162	1.319	1.074	0.144	372.10	0.760	0.406	1.031	1.341	0.094
355.92	0.049	0.026	1.799	0.992	0.021	361.00	0.397	0.179	1.258	1.092	0.144	373.00	0.779	0.426	1.026	1.367	0.089
356.21	0.071	0.038	1.747	0.993	0.033	361.63	0.435	0.193	1.209	1.120	0.147	376.65	0.835	0.507	1.016	1.396	0.068
356.26	0.077	0.040	1.722	0.995	0.037	362.18	0.457	0.207	1.215	1.121	0.151	378.75	0.867	0.556	1.006	1.449	0.055
356.61	0.106	0.055	1.680	0.998	0.053	362.73	0.485	0.218	1.181	1.144	0.150	379.95	0.881	0.587	1.007	1.450	0.050
356.65	0.108	0.055	1.659	0.998	0.053	363.85	0.528	0.241	1.158	1.161	0.148	381.50	0.899	0.622	0.997	1.498	0.038
357.05	0.142	0.069	1.560	1.007	0.069	364.55	0.556	0.255	1.135	1.183	0.145	382.60	0.912	0.652	0.997	1.527	0.035
357.08	0.146	0.072	1.580	1.008	0.074	365.22	0.580	0.268	1.120	1.198	0.142	384.10	0.926	0.691	0.997	1.528	0.029
357.54	0.175	0.086	1.548	1.010	0.085	365.98	0.608	0.284	1.101	1.224	0.138	386.80	0.949	0.763	0.991	1.569	0.014
357.59	0.183	0.089	1.536	1.014	0.090	366.27	0.622	0.290	1.088	1.245	0.135	388.50	0.962	0.810	0.989	1.608	0.007
357.95	0.209	0.100	1.482	1.022	0.099	367.13	0.645	0.306	1.075	1.260	0.129	390.57	0.979	0.878	0.992	1.772	0.004
358.20	0.230	0.110	1.464	1.029	0.110	367.85	0.663	0.318	1.064	1.270	0.122	394.18	1.000	1.000	1.000		0.000
$C_3H_7COOC_2H_5$ (1) + $CH_3CH_2CH(OH)CH_3$ (2)																	
372.39	0.000	0.000		1.000	0.000	376.78	0.418	0.285	1.137	1.048	0.081	385.63	0.811	0.633	0.997	1.239	0.038
372.83	0.042	0.032	1.412	0.988	0.003	377.21	0.448	0.305	1.119	1.059	0.082	386.27	0.830	0.659	0.995	1.256	0.035

Table 6. (Continued)

T/K	x_1	y_1	γ_1	γ_2	G^E/RT	T/K	x_1	y_1	γ_1	γ_2	G^E/RT	T/K	x_1	y_1	γ_1	γ_2	G^E/RT
						$C_3H_7COOC_2H_5$ (1) + $CH_3CH_2CH(OH)CH_3$ (2)											
373.06	0.073	0.053	1.364	0.991	0.014	377.70	0.476	0.324	1.102	1.068	0.081	386.70	0.843	0.675	0.991	1.281	0.031
373.31	0.105	0.075	1.326	0.994	0.024	378.01	0.497	0.338	1.091	1.078	0.081	387.17	0.856	0.694	0.990	1.293	0.028
373.66	0.142	0.101	1.301	0.996	0.034	378.37	0.518	0.351	1.076	1.089	0.079	387.75	0.874	0.718	0.986	1.338	0.024
373.91	0.171	0.120	1.278	1.000	0.042	379.15	0.561	0.383	1.060	1.106	0.077	388.65	0.896	0.755	0.985	1.368	0.019
374.16	0.199	0.138	1.254	1.005	0.049	379.90	0.599	0.416	1.053	1.119	0.076	389.32	0.911	0.785	0.988	1.377	0.017
374.40	0.222	0.154	1.244	1.007	0.054	380.20	0.614	0.428	1.046	1.127	0.074	390.02	0.928	0.815	0.987	1.438	0.014
374.72	0.253	0.174	1.225	1.012	0.060	381.10	0.652	0.460	1.031	1.147	0.068	390.22	0.937	0.825	0.984	1.546	0.012
375.01	0.278	0.192	1.218	1.014	0.065	382.15	0.698	0.501	1.015	1.181	0.061	391.12	0.954	0.865	0.988	1.578	0.009
375.27	0.303	0.207	1.196	1.022	0.069	382.85	0.726	0.529	1.010	1.199	0.057	391.62	0.968	0.89	0.988	1.831	0.008
375.63	0.335	0.228	1.175	1.031	0.074	383.28	0.741	0.545	1.006	1.211	0.054	392.53	0.982	0.931	0.993	2.011	0.006
376.04	0.365	0.249	1.165	1.035	0.078	384.72	0.787	0.597	0.994	1.245	0.042	394.18	1.000	1.000	1.000		0.000
376.38	0.393	0.266	1.145	1.045	0.080												

Table 7. Fitting Parameters for Different Equations Used, Mean Deviations of Temperature, and Vapor Composition and Standard Deviations of Gibbs Energy Function

			$\delta(T/\mathrm{K})$	$\delta(y_1)$	$s(G^E/RT)$
	$CH_3COOC_2H_5$ (1) + $CH_3CH(OH)CH_3$ (2)				
Margules	$A_{12} = 0.605$	$A_{21} = 0.623$	0.05	0.010	0.004
Van Laar	$A_{12} = 0.537$	$A_{21} = 0.653$	0.04	0.005	0.003
Wilson	$\Delta_{12} = -602.4$[a]	$\Delta_{21} = 2521.4$[a]	0.04	0.005	0.003
NRTL, $\alpha = 0.37$[b]	$\Delta g_{12} = 1665.1$[a]	$\Delta g_{21} = 220.8$[a]	0.03	0.005	0.003
UNIQUAC, $z = 10$	$\Delta u_{12} = 4822.8$[a]	$\Delta u_{21} = -1888.4$[a]	0.03	0.004	0.002
Redlich−Kister	$A_0 = 0.589$	$A_1 = 0.061$	0.04	0.005	0.003
eq 1, $k = 1.10$	$A_0 = 0.590$	$A_1 =$	0.04	0.005	0.003
	$CH_3COOC_2H_5$ (1) + $CH_3CH_2CH(OH)CH_3$ (2)				
Margules	$A_{12} = 0.380$	$A_{21} = 0.396$	0.03	0.009	0.007
Van Laar	$A_{12} = 0.303$	$A_{21} = 0.430$	0.01	0.003	0.003
Wilson	$\Delta_{12} = -480.6$[a]	$\Delta_{21} = 1757.8$[a]	0.01	0.004	0.004
NRTL, $\alpha = 0.52$[b]	$\Delta g_{12} = 1512.9$[a]	$\Delta g_{21} = -246.2$[a]	0.01	0.003	0.004
UNIQUAC, $z = 10$	$\Delta u_{12} = 4486.6$[a]	$\Delta u_{21} = -2128.4$[a]	0.01	0.002	0.002
Redlich−Kister	$A_0 = 0.356$	$A_1 = 0.066$	0.01	0.003	0.003
eq 1, $k = 1.19$	$A_0 = 0.359$	$A_1 =$	0.01	0.003	0.003
	$C_2H_5COOC_2H_5$ (1) + $CH_3CH(OH)CH_3$ (2)				
Margules	$A_{12} = 0.545$	$A_{21} = 0.524$	0.04	0.006	0.005
Van Laar	$A_{12} = 0.541$	$A_{21} = 0.577$	0.04	0.005	0.005
Wilson	$\Delta_{12} = -881.2$[a]	$\Delta_{21} = 2701.8$[a]	0.04	0.004	0.005
NRTL, $\alpha = 0.27$[b]	$\Delta g_{12} = 1205.7$[a]	$\Delta g_{21} = 522.4$[a]	0.04	0.004	0.005
UNIQUAC, $z = 10$	$\Delta u_{12} = 4636.8$[a]	$\Delta u_{21} = -1871.5$[a]	0.03	0.005	0.005
Redlich−Kister	$A_0 = 0.559$	$A_1 = 0.019$	0.04	0.005	0.005
eq 1, $k = 1.03$	$A_0 = 0.559$	$A_1 =$	0.04	0.005	0.005
	$C_2H_5COOC_2H_5$ (1) + $CH_3CH_2CH(OH)CH_3$ (2)				
Margules	$A_{12} = 0.384$	$A_{21} = 0.464$	0.11	0.018	0.007
Van Laar	$A_{12} = 0.260$	$A_{21} = 0.518$	0.07	0.007	0.004
Wilson	$\Delta_{12} = -1716.6$[a]	$\Delta_{21} = 3521.4$[a]	0.07	0.007	0.004
NRTL, $\alpha = 0.62$[b]	$\Delta g_{12} = 2322.4$[a]	$\Delta g_{21} = -680.6$[a]	0.07	0.007	0.004
UNIQUAC, $z = 10$	$\Delta u_{12} = 5093.7$[a]	$\Delta u_{21} = -2414.8$[a]	0.05	0.008	0.004
Redlich−Kister	$A_0 = 0.349$	$A_1 = 0.127$	0.06	0.007	0.004
eq 1, $k = 0.81$	$A_0 = 0.135$	$A_1 = 0.404$	0.06	0.008	0.004
	$C_3H_7COOC_2H_5$ (1) + $CH_3CH(OH)CH_3$ (2)				
Margules	$A_{12} = 0.551$	$A_{21} = 0.465$	0.02	0.003	0.007
Van Laar	$A_{12} = 0.593$	$A_{21} = 0.497$	0.02	0.005	0.010
Wilson	$\Delta_{12} = -708.9$[a]	Δ_{21} 2524.3a	0.02	0.004	0.009
NRTL, $\alpha = 0.39$[b]	$\Delta g_{12} = 496.1$[a]	$\Delta g_{21} = 1284.8$[a]	0.02	0.004	0.009
UNIQUAC, $z = 10$	$\Delta u_{12} = 4513.6$[a]	$\Delta u_{21} = -1823.9$[a]	0.02	0.005	0.009
Redlich−Kister	$A_0 = 0.539$	$A_1 = -0.053$	0.02	0.005	0.010
eq 1, $k = 0.91$	$A_0 = 0.541$	$A_1 =$	0.02	0.005	0.010
	$C_3H_7COOC_2H_5$ (1) + $CH_3CH_2CH(OH)CH_3$ (2)				
Margules	$A_{12} = 0.309$	$A_{21} = 0.305$	0.03	0.006	0.006
Van Laar	$A_{12} = 0.305$	$A_{21} = 0.317$	0.03	0.006	0.007
Wilson	$\Delta_{12} = -892.8$[a]	$\Delta_{21} = 1931$[a]	0.03	0.006	0.007
NRTL, $\alpha = 0.54$[b]	$\Delta g_{12} = 714.3$[a]	$\Delta g_{21} = 318.3$[a]	0.03	0.006	0.007
UNIQUAC, $z = 10$	$\Delta u_{12} = 3897.8$[a]	$\Delta u_{21} = -2074.4$[a]	0.02	0.005	0.005
Redlich−Kister	$A_0 = 0.311$	$A_1 = 0.006$	0.03	0.006	0.007
eq 1, $k = 0.56$	$A_0 = 0.110$	$A_1 = 0.368$	0.02	0.004	0.005

[a] All parameters in $J \cdot mol^{-1}$. [b] Obtained by fit.

for T, δT, vapor concentration, δy_i, and the standard deviation of the Gibbs free energy, $s(G^E/RT)$. The goodness of fit was rather similar in all cases.

Figures 3 and 4 plot the fitting curves for the experimental values for each of the mixtures considered (see Table 6), using an expression similar to eq 1. The figures present comparisons of the concentration and temperature values in the literature for the system ethyl ethanoate (1) + propan-2-ol (2) at 101.32 kPa and reveal large discrepancies from the values presented here. For $(y_1 - x_1)$ the largest differences appeared at a concentration of around $x_1 = 0.25$, whereas in the temperature plots, the greatest differences, around 2 K, appeared at a concentration of around $x_1 = 0.70$. Nevertheless, all the values reported in

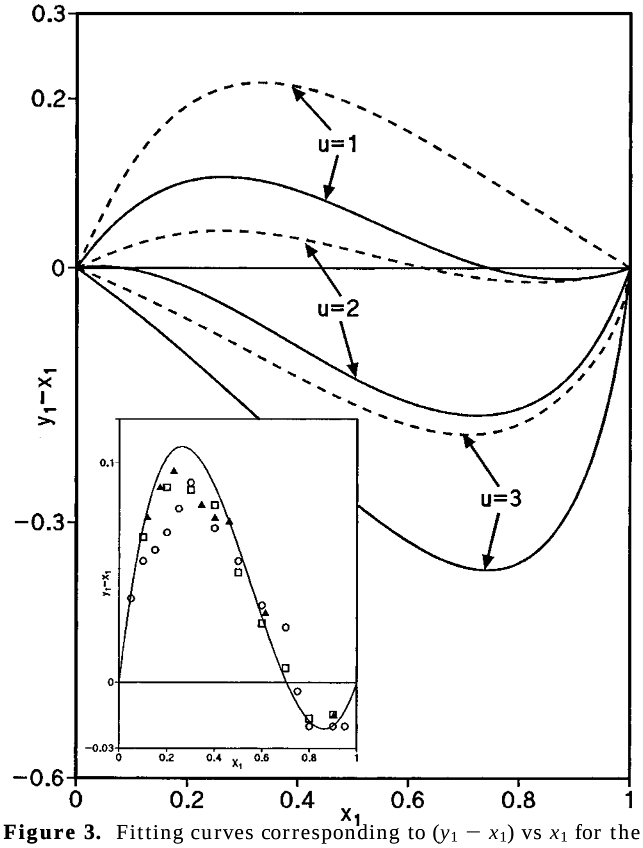

Figure 3. Fitting curves corresponding to ($y_1 - x_1$) vs x_1 for the mixtures $C_uH_{2u+1}CO_2C_2H_5$ (1) + alkan-2-ol (2): (—), propan-2-ol; (- - -), butan-2-ol. Inset corresponds to the comparison of our experimental curve with the values from literature for ethyl ethanoate (1) + propan-2-ol (2): ▲, Murti and van Winkle (1958); □, Nishi (1972); ○, Rajendran et al. (1991).

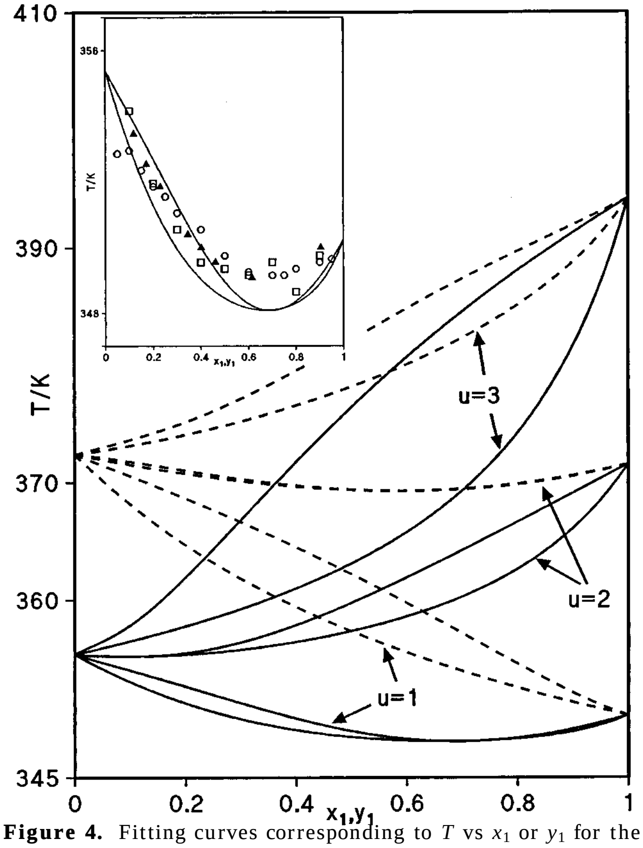

Figure 4. Fitting curves corresponding to T vs x_1 or y_1 for the mixtures $C_uH_{2u+1}CO_2C_2H_5$ (1) + alkan-2-ol (2): (—), propan-2-ol; (- - -), butan-2-ol. Inset corresponds to the comparison of our experimental curve with the values from literature for the liquid phase of ethyl ethanoate (1) + propan-2-ol (2): ▲, Murti and van Winkle (1958); □, Nishi (1972); ○, Rajendran et al. (1991).

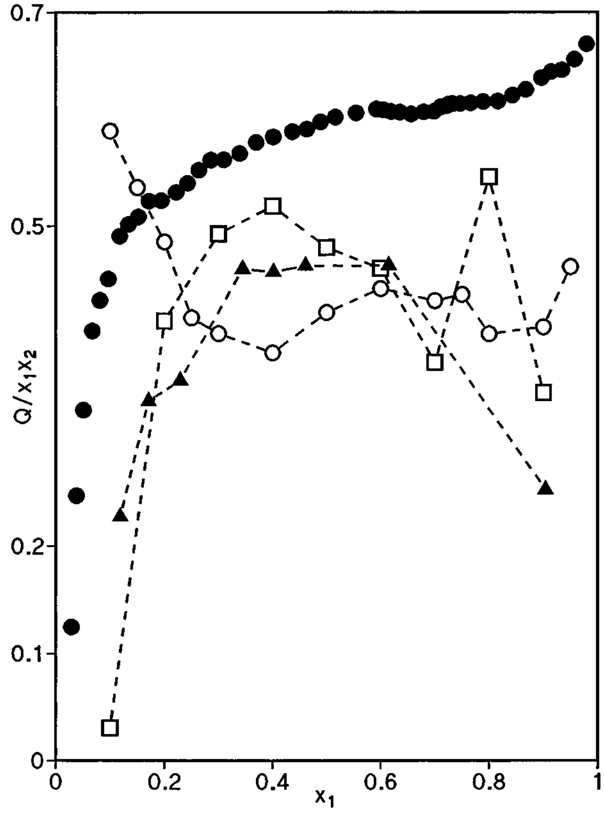

Figure 5. Comparison between the curves of the fuction $Q = G^E/RT$, in the form Q/x_1x_2 vs x_1, obtained by us, ●, and the values from literature: ▲, Murti and van Winkle (1958); □, Nishi (1972); ○, Rajendran et al. (1991).

Table 8. Coefficients of Eq 7 and Mean Deviation of γ_i and Standard Deviation for G^E/RT

system	k_g	a_0	a_1	b_0	$\delta\gamma_i$	$s(G^E/RT)$
Ethyl Ethanoate (1)						
+ propan-2-ol (2)	0.735	0.351	0.416	0.112	0.009	0.002
+ butan-2-ol (2)	1.053	0.361		0.123	0.017	0.002
Ethyl Propanoate (1)						
+ propan-2-ol (2)	0.855	0.523		0.211	0.013	0.003
+ butan-2-ol (2)	0.889	0.281		0.321	0.009	0.002
Ethyl Butanoate (1)						
+ propan-2-ol (2)	0.890	0.584		0.209	0.009	0.003
+ butan-2-ol (2)	1.068	0.387		−0.015	0.020	0.002

the literature for the same mixture by Murti and van Winkle (1958), Nishi (1972), and Rajendran et al. (1991) were treated like ours, and all of them were consistent using the point-to-point method recommended by Fredenslund et al. (1977). An alternative was to represent the nondimensional function of Gibbs energy, $Q = G^E/RT$, of the form Q/x_1x_2 vs x_1 for the mixtures from literature. Figure 5 shows the differences among the various authors.

Figure 6a−f graphically represent the values from the columns in Table 6 for γ_i and G^E/RT vs x_1 using the correlation described in the following section. The mixtures containing ethanoates displayed a small maximum in the γ_i values at low concentrations of the alkan-2-ol. This finding has been reported in previous papers and has not yet been satisfactorily explained but may be attributable to difficulties involving pseudoreaction between the components: on the one hand, the rupture of the hydrogen bonds in the alkanol molecules and the formation of associated polymers, and on the other hand, the opposite, exothermic effect, caused by the formation of ester + alkanol esterification complexes. Therefore, the virial coefficients were also calculated using the method proposed by Hayden and O'Connell (1975) considering a term includ-

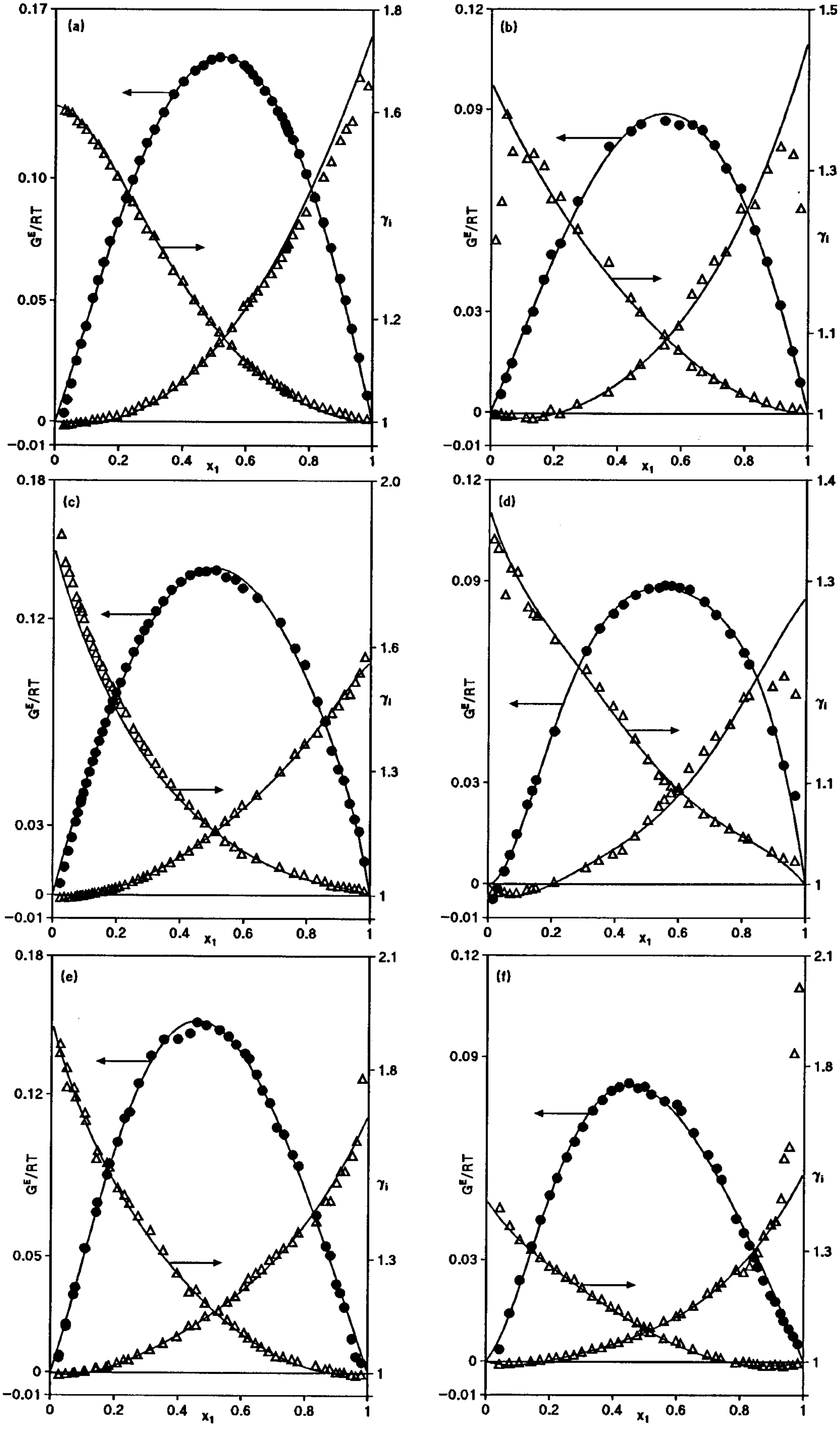

Figure 6. Experimental results of G^E/RT (●) and γ_i (△) vs x_1 and the corresponding fitting curves for the binary mixtures ethyl ester (1) + alkan-2-ol (2): (a, c, e) ethyl ethanoate, propanoate, butanoate + propan-2-ol; (b, d, f) ethyl ethanoate, propanoate, butanoate + butan-2-ol.

Table 9. Average Mean Deviations, δ, and Errors, e, Obtained Applying Different Models to the Mixtures Ethyl Ester (1) + Alkan-2-ol (2)

	ASOG	Mod-UNIFAC	UNIFAC			
	OH/COO[a]	OH/COOC[b]	CCOH/COOC[c]	COH/COO[d]	OH/COOC[e]	OH/COO[f]
Ethyl Ethanoate (1) + Propan-2-ol (2)						
δy_1	0.016	0.006	0.011	0.007	0.024	0.010
δT/K	0.67	0.48	0.47	0.26	1.46	0.28
$e(\gamma)$	5.96	2.46	4.36	1.89	10.90	3.44
(x_{az}, T_{az})	(0.635, 347.51)	(0.709, 348.71)	(0.652, 347.69)	(0.678, 348.41)	(0.638, 346.44)	(0.658, 347.93)
Ethyl Ethanoate (1) + Butan-2-ol (2)						
δy_1	0.021	0.004	0.018	0.013	0.028	0.013
δT/K	1.42	0.27	1.24	0.86	1.91	0.82
$e(\gamma)$	12.22	3.40	10.61	7.82	16.33	7.48
Ethyl Propanoate (1) + Propan-2-ol (2)						
δy_1	0.011	0.005	0.015	0.006	0.028	0.010
δT/K	0.74	0.35	0.98	0.15	1.73	0.70
$e(\gamma)$	5.40	2.26	7.32	2.25	13.86	5.02
(x_{az}, T_{az})	(0.144, 354.56)	(0.093, 354.94)	(0.157, 354.62)	(0.040, 355.06)	(0.221, 354.02)	(0.134, 354.70)
Ethyl Propanoate (1) + Butan-2-ol (2)						
δy_1	0.024	0.017	0.025	0.018	0.031	0.021
δT/K	1.29	0.89	1.60	0.81	2.14	1.15
$e(\gamma)$	11.28	8.01	13.05	7.72	17.32	9.97
(x_{az}, T_{az})	(0.505, 367.66)	(0.539, 368.17)	(0.536, 367.19)	(0.518.368.32)	(0.546, 366.45)	(0.525, 367.85)
Ethyl Butanoate (1) + Propan-2-ol (2)						
δy_1	0.009	0.004	0.018	0.006	0.028	0.012
δT/K	0.85	0.31	1.63	0.30	2.67	1.20
$e(\gamma)$	4.64	1.77	8.42	3.12	15.85	5.82
Ethyl Butanoate (1) + Butan-2-ol (2)						
δy_1	0.013	0.007	0.022	0.007	0.028	0.015
δT/K	1.46	0.94	2.30	0.91	3.03	1.70
$e(\gamma)$	7.22	4.83	11.69	4.50	16.39	8.38

[a] Tochigi et al. (1990). [b] Gmehling et al. (1993). [c] Fredenslund et al. (1977). [d] Fredenslund et al. (1975). [e] Hansen et al. (1991). [f] Macedo et al. (1983). [g]

$$e(\gamma) = (1/2)\sum_{i=1}^{2}\sum_{j=1}^{N}|(\gamma_{i,j}^{\text{exp}} - \gamma_{i,j}^{\text{cal}})/\gamma^{\text{exp}}{}_{i,j}|100/N;\ \delta(y_1) = \sum_{j=1}^{N}|(y_{l,j}^{\text{exp}} - y_{l,k}^{\text{cal}})|/N;\ \delta(T) = \sum_{i=1}^{N}|(T_{i,\text{exp}} - T_{i,\text{cal}})|/N$$

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ing the chemical interaction; however, the differences with respect to the values in Table 6 were not significant.

The excess enthalpies were calculated from $H^E = -RT^2[\partial(G^E/RT)/\partial T]_p$. The literature has yielded H_m^E values for the mixture formed by ethyl ethanoate + propan-2-ol at three temperatures, 298.15 K, 303.15 K, and 308.15 K (Nagata et al., 1975; Grolier and Viallard, 1971; Ortega, 1996; Rajendran et al., 1991), and for the mixture consisting of ethyl ethanoate + butan-2-ol at one temperature, 298.15 K (Ortega, 1996). The NRTL and Wilson equation gives values that differ by 80% for the two mixtures; the errors with UNIQUAC model were higher. Therefore, another option was to fit the parameters to the temperature using the experimental enthalpy values. In Soto et al. (1997), an attempt was made to establish the suitability of using the proposed polynomial equation, similar to eq 1, in correlating the values. The activity coefficients and Q are related by

$$\ln \gamma_1 = Q + x_2 \ln(\gamma_1/\gamma_2) \quad \text{and} \quad \ln \gamma_2 = Q - x_1 \ln(\gamma_1/\gamma_2) \tag{4}$$

where

$$\ln(\gamma_1/\gamma_2) = [\partial(G^E/RT)/\partial x_1] + (H^E/RT^2)(\partial T/\partial x_1) \tag{5}$$

with $Q = G^E/RT$ being represented by a function similar to eq 1.

Logically, the direct correlations for this excess function vs concentration, with no restrictions other than to minimize the deviation values for Q, will give better results than when the correlation is conditioned on other variables, as in the software used herein. The literature does not report sufficient values at different temperatures to obtain an adequate plot for the enthalpic term, which was therefore replaced by a simple form of eq 1 truncated at the first term. Chao (1959) made a similar modification using the Redlich−Kister equation, so introducing this consideration into eq 5 and regrouping yields

$$\ln(\gamma_1/\gamma_2) = k_g(z_1/x_1)^2[(1 - 2z_1)\sum_i a_i z_1^i + z_1 z_2 \sum_i (i + 1)a_{i+1} z_1^i] + z_1 z_2 \sum_i b_i z_1^i \tag{6}$$

where $z_1 = x_1/(x_1 + k_g x_2)$ and a_i, k_g, and b_i are parameters appearing in Table 8 determined under the same conditions and requirements as the parameters given in Table 7. Tailoring eq 5 to a specific binary mixture, taking only two coefficients for a_i and one for b_i, allows it to be rewritten as

$$\ln(\gamma_1/\gamma_2)_p = k_g(z_1/x_1)^2[(1 - 2z_1)(a_0 + a_1 z_1) + z_1 z_2 a_1] + b_0 z_1 z_2 \tag{7}$$

The parameters a_i shown in Table 8 are not the same as the ones in Table 7 because of the added polynomial term. On the other hand, use of the summation term yields a better fit, in some cases with a smaller number of parameters. The standard deviation values for the γ_i values in Table 8 support this. In this case the goodness of fit, $s(G^E/RT)$, is the same as the one that would have been obtained from directly fitting the adimensional Gibbs free energy function on the basis of composition. It can therefore be concluded that the function shown in eq 7 should be suitable for correlating the adimensional Gibbs free energy function and the activity coefficients concurrently.

Azeotropes. Azeotropes were located at the following coordinates in the binary systems: for ethyl ethanoate (1) + propan-2-ol (2) at $x_1 = 0.707$, $T = 348.1$ K; for ethyl propanoate (1) + propan-2-ol (2) at $x_1 = 0.092$, $T = 355.2$ K; for ethyl propanoate (1) + butan-2-ol (2) at $x_1 = 0.628$, $T = 369.3$ K. The literature contains no references to any azeotropes in the system consisting of ethyl propanoate + propan-2-ol, but Gmehling et al. (1994) reported values estimated by Lecat, namely, $x_{\mathrm{az,ester}} = 0.450$, $T_{\mathrm{az}} = 368.9$ K, for ethyl propanoate + butan-2-ol. Those values differ considerably from the values reported here.

Using reduced coordinate sets, the numerous literature values for the azeotropes of the ethyl ethanoate + propan-2-ol mixture at different pressures were represented, with their regression line being used as the corresponding geometric means of the individual values, i.e., $p_{cij} = (p_{ci}p_{cj})^{1/2}$ and $T_{cij} = (T_{ci}T_{cj})^{1/2}$, as the mixing rules for the critical temperature and pressure. The inset to Figure 4 shows the differences in temperature for that mixture between the literature values at 101.32 kPa and the value calculated in this study. The inset to Figure 2 shows the convergence between the regression lines for the vapor pressures for the pure components. Theoretically, at least, the lines must go through the point (1, 0). The azeotropic line, obtained by regression for the mixture of ethyl ethanoate + propan-2-ol plotted on the reduced coordinate set, was

$$\log p_{\mathrm{r}} = (-3.594/T_{\mathrm{r}}) + 3.700 \tag{8}$$

and also showed a moderate convergence with the others. Assuming that the azeotropes reported by literature [Murti and van Winkle (1958) at 25.7 and 57.8 kPa; Nagata et al. (1975) at 48.4 kPa] are correct, if instead of the experimental value presented here, the closest literature value, the one calculated by Lecat [see Gmehling et al. (1994)] is used, then the azeotropic line and that of vapor pressure for ethyl butanoate would be almost parallel. The acentric pseudofactor for the azeotropic line, calculated from eq 8, gave a different result in comparison with that corresponding to a mean value of the individuals acentric factors.

Prediction of VLE. The experimental values shown in Table 6 were substituted in several known theoretical models, namely, the ASOG model (Tochigi et al., 1990) and the original version of the UNIFAC model (Fredenslund et al. 1975), as well as the version subsequently developed by Gmehling et al. (1993). Table 9 gives the results obtained using the different models along with the deviations in the mole fraction of the vapor phase, δy_1, and temperature, δT, recalculated using the bubble method put forward by Prausnitz et al. (1980).

On the whole, Gmehling et al.'s version of the UNIFAC model (1993) yielded the best prediction for all the mixtures considered here, with a mean overall percentage error of less than 4% for the activity coefficients, although the error in the prediction for the mixture consisting of ethyl propanoate + butan-2-ol was 7%. As in the other cases previously considered by our laboratory, the worst estimates of the original version of the UNIFAC model published by Hansen et al. (1991) yielded a mean error on the order of 14% for the six mixtures considered here.

The coordinates for the azeotrope estimated for the system formed by ethyl ethanoate + propan-2-ol using the various models tested were not very good, although the best results were achieved using Gmehling et al.'s version of the UNIFAC model (1993). For the system composed of ethyl propanoate + propan-2-ol, the best estimates were obtained using Fredenslund et al.'s (1975) and Gmehling et al.'s (1993) versions of the UNIFAC model. Finally, for the system consisting of ethyl propanoate + butan-2-ol, the three models estimated considerably different coordinates for the singular point than the experimental value obtained, with differences in temperature of up to 2 K. On the whole, the best/worst approximations to the experimentally determined azeotropes were achieved by the models with the lowest/highest mean in the errors in their predictions of γ_i.

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