

Densities and Vapor–Liquid Equilibrium Values for Binary Mixtures Composed of Methanol + an Ethyl Ester at 141.3 kPa with Application of an Extended Correlation Equation for Isobaric VLE Data

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Vapor–liquid equilibrium data for binary systems containing methanol and ethyl esters, from methanoate to butanoate, are measured in a small recirculating still at 141.3 kPa and reported. Employing the same equilibrium still, the experimental vapor pressures are obtained for the ethyl esters considered here and correlated with a suitable equation. The densities and derived excess volumes for the same mixtures are also reported at 298.15 K. Azeotropes are found in the mixtures of methanol (1) + ethyl methanoate (2) and + ethyl ethanoate (2) at $x_1 = 0.337$, $T = 333.7$ K and $x_1 = 0.742$, $T = 343.8$ K, respectively. The data are correlated by using a new equation containing temperature-dependent coefficients. The estimates of various quantities including the excess enthalpies appear to be satisfactory. Activity coefficients calculated from experimental values are compared with those predicted by ASOG and UNIFAC group-contribution models.

Introduction

Methanol has been accorded special attention in the theoretical and experimental work carried out by our laboratory for the purpose of analyzing the thermodynamic properties of binary mixtures of alkyl esters and alkanols. For that reason, in previous papers, Blanco and Ortega (1996a,b) published experimental values for mixtures of methanol + an *n*-alkane and methanol + a methyl ester, respectively. The present paper sets out the experimental vapor–liquid equilibrium (VLE) values for binary mixtures of methanol + an ethyl ester (from methanoate to butanoate) at 141.3 kPa, along with the density values recorded at different methanol concentrations and the corresponding excess volumes. Isobaric VLE values for the system methanol + ethyl ethanoate have been found in the literature, but always at lower pressures than the working pressure used in this study; see Gmehling et al. (1996), Vol 2a, pp 154–167, Vol. 2e, p 108. Literature values for the systems methanol + ethyl methanoate and methanol + ethyl ethanoate showing azeotropes, see Gmehling et al. (1994), have also been found and are presented for purposes of comparison. Use of a modified polynomial equation with temperature-dependent parameters already employed earlier for correlation of the VLE values is proposed.

Finally, the VLE values for the mixtures considered were predicted using the ASOG and UNIFAC group-contribution models.

Experimental Section

Materials. The components used were the highest commercial grade available from the manufacturer, Fluka. Before use components were degassed by ultrasound for several hours and then dried on a molecular sieve (Fluka, 0.3 nm). In other laboratory we have checked the purity of ethyl esters using a HP-6890 GC equipped with a FID and a capillary column HP-Wax; injector and detector

temperatures were 323 and 573 K, respectively. Any significant impurities were observed in those analyses, and the results were coincident with those shown by supplier. The physical properties, normal boiling temperature, $T_{b,i}$, density, ρ , at 298.15 K, and refractive index, $n(D, 298.15$ K), determined for the ethyl esters and the methanol are shown in Table 1.

Equipment and Procedure. A small equilibrium still in which both phases were refluxed was used. The details of the equipment and support systems have been described in Ortega et al. (1986b). The uncertainties in the measured temperatures and pressures were ± 0.02 K and ± 0.2 kPa, respectively.

The composition of the liquid and vapor phases was determined by densimetry using standard curves for the mixtures considered, prepared earlier, $\rho = \rho(x)$. The density measurements were effected using an Anton Paar model DMA-55 thermostatted digital densimeter with a precision of ± 0.02 kg·m⁻³. The correlations of the density and concentration values for the methanol (1) + ethyl ester (2) mixtures were carried out using simple polynomial equations of the type $\rho = \sum a_i x_i^i$, and these were then used to calculate the concentrations in each of the equilibrium states. The precision of the calculation of the mole fractions for both the liquid phase and the vapor phase of the methanol was better than ± 0.002 units.

Results and Discussion

Densities and Excess Volumes. The density, ρ , values were determined at (298.15 ± 0.01) K over the entire range of concentrations for each of the methanol (1) + ethyl ester (2) binary systems, and the excess values, V_m^E , were then calculated (see Table 2) to validate the values of the data pairs (x, ρ). The precision of the calculations was $\pm 10^{-4}$ units for the mole fraction and $\pm 2 \cdot 10^{-9}$ m³·mol⁻¹ for the V_m^E values. The data pairs were correlated using a power

Table 1. Physical Properties of Pure Compounds at Atmospheric Pressure

	purity/mass %	$T_b, /K$		$\rho(298.15 \text{ K})/\text{kg}\cdot\text{m}^{-3}$		$n \text{ (D, 298.15 K)}$		ω	
		exptl	lit.	exptl	lit.	exptl	lit.	calcd	lit.
methanol	"puriss. p.a." >99.5	337.42	337.85 ^a 337.69 ^b	786.79	786.64 ^{a,b} 787.45 ^g	1.3266	1.3265 ^{a,b,g}	0.561	0.566 ^g
ethyl methanoate	"purum" >98	327.45	327.46 ^{a,c,g}	915.82	915.30 ^{a,c} 916.50 ^g	1.3581	1.3575 ^{a,c,g}	0.273	0.285 ^g
ethyl ethanoate	"puriss. p.a." >99	350.13	350.26 ^a 350.21 ^{d,g}	894.27	894.55 ^a 894.00 ^d	1.3700	1.3698 ^a 1.3704 ^{d,g}	0.358	0.361 ^g
ethyl propanoate	"puriss." >99	372.15	372.25 ^{a,e,g}	884.02	884.00 ^{a,e} 884.42 ^g	1.3815	1.3814 ^{a,e,g}	0.391	0.394 ^g
ethyl butanoate	"purum" >98	394.18	394.70 ^a 394.65 ^{f,g}	873.54	873.94 ^a 873.70 ^f	1.3898	1.3900 ^{f,g}	0.412	0.419 ^g

^a Riddick et al., 1986. ^b TRC a-5030, 1967. ^c TRC a-5520, 1969. ^d TRC a-5550, 1969. ^e TRC a-5580, 1969. ^f TRC a-5610, 1976. ^g Daubert and Danner, 1984.

Table 2. Densities, ρ , and Excess Volumes, V_m^E , for Binary Systems of Methanol (1) + Ethyl Esters (2) at 298.15 K

x_1	$\rho/\text{kg}\cdot\text{m}^{-3}$	$10^9 \cdot V_m^E/\text{m}^3\cdot\text{mol}^{-1}$	x_1	$\rho/\text{kg}\cdot\text{m}^{-3}$	$10^9 \cdot V_m^E/\text{m}^3\cdot\text{mol}^{-1}$
Methanol (1) + Ethyl Methanoate (2)					
0.0568	912.54	-45	0.6020	861.86	-127
0.1413	906.77	-71	0.6449	855.95	-121
0.2169	901.16	-93	0.6807	850.81	-120
0.2356	899.67	-97	0.7066	846.73	-109
0.2519	898.39	-104	0.7453	840.58	-107
0.3222	892.48	-124	0.7852	833.78	-101
0.3843	886.60	-125	0.8203	827.33	-92
0.4268	882.39	-131	0.8631	818.88	-76
0.4701	877.79	-133	0.9175	807.06	-50
0.5192	872.21	-133	0.9677	795.23	-34
0.5763	865.24	-132			
Methanol (1) + Ethyl Ethanoate (2)					
0.0650	891.46	-21	0.5810	856.05	-69
0.1154	889.03	-27	0.6077	853.27	-68
0.2045	884.40	-44	0.6567	847.73	-63
0.2521	881.69	-53	0.6903	843.66	-62
0.2665	880.80	-52	0.7218	839.55	-58
0.3009	878.69	-59	0.7855	830.36	-49
0.3376	876.28	-63	0.8426	820.97	-40
0.3794	873.35	-65	0.8867	812.83	-34
0.4274	869.76	-68	0.9262	804.60	-21
0.5327	860.78	-71	0.9654	795.66	-1
Methanol (1) + Ethyl Propanoate (2)					
0.0398	882.68	-8	0.6463	846.46	-39
0.1887	876.93	-31	0.7261	837.57	-34
0.2179	875.61	-32	0.7671	832.24	-28
0.2557	873.86	-37	0.7797	830.46	-24
0.3153	870.87	-44	0.8079	826.38	-24
0.3958	866.26	-45	0.8627	817.39	-18
0.4609	862.06	-50	0.8898	812.38	-14
0.5284	857.08	-49	0.9419	801.51	-9
Methanol (1) + Ethyl Butanoate (2)					
0.0400	872.49	-6	0.5707	848.78	-31
0.0875	871.15	-12	0.6416	843.10	-23
0.2049	867.37	-22	0.6776	839.86	-23
0.1671	868.64	-16	0.7001	837.63	-19
0.2459	865.87	-26	0.7733	829.47	-17
0.3199	862.88	-31	0.8309	821.65	-14
0.3754	860.36	-34	0.8656	816.13	-9
0.4227	857.97	-34	0.9110	807.92	-7
0.4731	855.15	-33	0.9594	797.39	-2
0.5122	852.77	-33			

series for the variable z , defined as $z = x_1/(x_1 + k_v x_2)$, where $k_v = V_2^0/V_1^0$ and took on a constant value for each mixture equal to the quotient of the molar volumes of the pure components at the working temperature. The polynomial equation employed was

$$10^9 V_m^E/\text{m}^3\cdot\text{mol}^{-1} = x_1 x_2 \sum b_i z^i \quad (1)$$

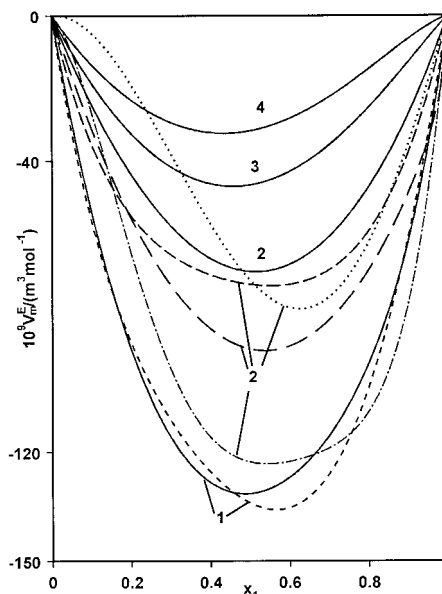


Figure 1. Experimental curves (solid lines) obtained at 298.15 K for CH_3OH (1) + $\text{C}_{u-1}\text{H}_{2u-1}\text{CO}_2\text{C}_2\text{H}_5$ (2) and those from literature. (···) Akita and Yoshida (1963); (---), Nakanishi and Shirai (1970); (—), Grolier and Viillard (1971); (— · —), Nikam et al. (1996); (- - -), Ortega et al. (1986a). Labels indicate u -values.

Table 3. Coefficients, b_i , k_v , and Standard Deviation Obtained Using Eq 1 to Correlate Excess Volumes

system	$k_v = V_2^0/V_1^0$	b_0	b_1	b_2	$10^9 \cdot s(V_m^E)$
methanol (1) + ethyl methanoate (2)	1.99	-628	567	-781	5
methanol (1) + ethyl ethanoate (2)	2.42	-269	-42		2
methanol (1) + ethyl propanoate (2)	2.84	-210	88		2
methanol (1) + ethyl butanoate (2)	3.27	-153	110		2

The values of the coefficients, b_i , were calculated by linear regression of the experimental data with minimization of the standard deviation, $s(V_m^E)$, values and are listed in Table 3. The literature contains values for this excess magnitude for the systems methanol (1) + ethyl methanoate (2) (Ortega et al., 1986a) and methanol (1) + ethyl ethanoate (Akita and Yoshida, 1963; Grolier and Viillard, 1971; Nakanishi and Shirai, 1970; Nikam et al., 1996). Figure 1 graphically presents the experimental values determined in this study and the fitted curves plotted using eq 1, along with the literature curves for comparison. For the system methanol (1) + ethyl methanoate (2), the V_m^E

Table 4. Experimental Vapor Pressures for Pure Ethyl Esters

T/K	p_r^o/kPa	T/K	p_r^o/kPa	T/K	p_r^o/kPa
Ethyl Methanoate					
307.53	48.10	322.55	85.28	329.69	109.44
308.86	50.80	323.45	88.03	330.41	112.19
310.13	53.44	324.21	90.45	331.18	115.08
311.35	55.84	325.10	93.28	331.75	117.40
312.57	58.66	325.83	95.75	332.53	120.53
313.71	61.39	326.44	97.84	332.91	122.14
314.69	63.74	326.94	99.52	333.77	125.76
315.86	66.59	327.29	100.74	334.40	128.47
316.99	69.50	327.59	101.77	334.89	130.63
317.95	72.02	327.87	102.76	335.56	133.49
318.96	74.69	328.24	104.06	336.17	136.16
319.93	77.38	328.60	105.41	336.77	138.95
320.82	79.98	328.97	106.74	337.48	142.19
321.65	82.43				
Ethyl Ethanoate					
334.81	60.06	346.51	90.03	353.97	114.92
335.66	61.96	347.16	91.99	354.49	116.82
336.54	63.97	348.55	96.31	355.01	118.76
337.47	66.16	348.94	97.59	355.55	120.79
338.29	67.94	349.40	99.07	356.03	122.60
339.11	69.91	349.87	100.63	356.56	124.69
339.89	71.87	350.35	102.09	357.08	126.74
340.77	74.12	350.48	102.75	357.61	128.79
341.55	76.10	350.87	104.09	358.08	130.68
342.29	78.08	351.25	105.34	358.55	132.55
343.06	80.12	351.66	106.72	359.05	134.64
343.76	82.07	352.23	108.70	359.55	136.77
344.47	84.05	352.78	110.62	360.01	138.71
345.17	86.05	353.48	113.12	360.43	140.55
345.84	88.02				
Ethyl Propanoate					
349.56	47.74	368.73	91.05	378.41	122.66
351.01	50.22	369.60	93.60	379.13	125.34
352.45	52.85	370.52	96.33	379.85	127.99
353.82	55.55	371.00	97.80	380.58	130.67
355.25	58.29	371.56	99.43	381.25	133.30
356.67	61.27	372.00	100.80	381.95	136.08
357.99	64.02	372.49	102.55	382.55	138.53
359.25	66.68	372.96	104.01	383.24	141.32
360.42	69.32	373.41	105.37	383.90	144.03
361.57	72.01	373.85	106.78	384.52	146.65
362.62	74.64	374.64	109.32	385.15	149.37
363.70	77.31	375.45	112.00	385.77	152.03
364.71	79.99	375.83	113.33	386.38	154.75
365.77	82.87	376.23	114.68	386.96	157.28
366.79	85.61	377.02	117.37	387.53	159.74
367.79	88.38	377.73	120.03		
Ethyl Butanoate					
374.94	55.78	390.40	90.69	399.41	117.80
376.40	58.54	391.37	93.26	400.17	120.34
377.86	61.30	392.05	95.15	400.95	122.97
379.14	63.96	392.73	97.13	401.73	125.76
380.48	66.77	393.53	99.36	402.62	128.96
381.71	69.43	394.16	101.21	403.20	130.93
382.79	71.84	394.18	101.28	403.76	133.04
384.06	74.73	395.22	104.32	404.53	135.96
385.21	77.36	395.78	106.05	405.28	138.76
386.23	79.84	396.92	109.53	405.93	141.18
387.41	82.81	398.17	113.66	406.68	144.01
388.37	85.14	398.50	114.64	407.37	146.78
389.30	87.74	399.22	116.98		

values showed good agreement with the values determined previously at our laboratory (Ortega et al., 1986a), with mean estimated differences of 4%, although small difference exists for the concentration corresponding to the minima of both curves (0.51 and 0.56). However, for the system methanol (1) + ethyl ethanoate (2), there were discrepancies with respect to the literature values. Accordingly, the values determined in this study differed by 20% from those reported by Nakanishi and Shirai (1970), by 39% from those published by Grolier and Viillard

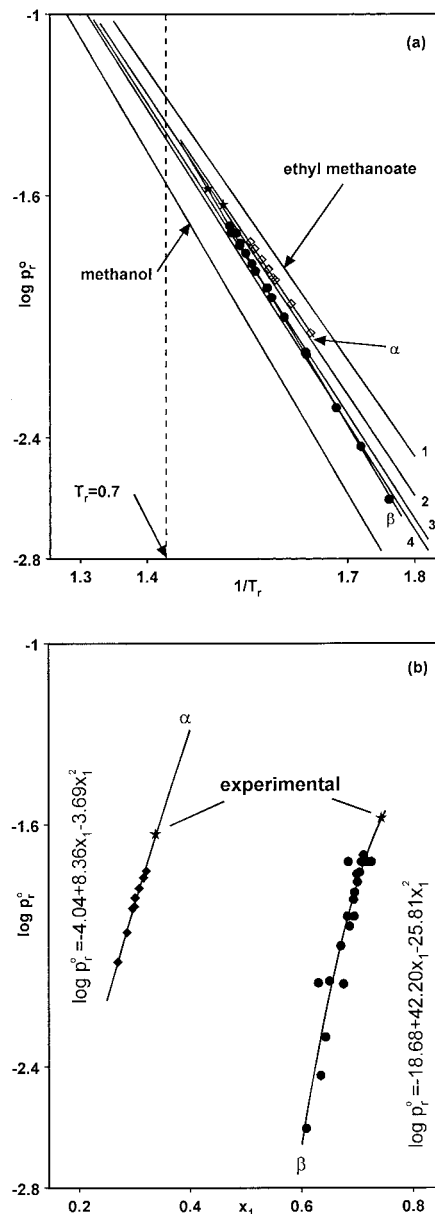


Figure 2. Experimental vapor pressure lines using reduced coordinates. (a) Plot of $\log p_r^o$ vs $1/T_r$ for pure compounds: (1) ethyl methanoate, $\log p_r^o = -3.203/T_r + 3.302$; (2) ethyl ethanoate, $\log p_r^o = -3.322/T_r + 3.388$; (3) ethyl propanoate, $\log p_r^o = -3.437/T_r + 3.519$; (4) ethyl butanoate, $\log p_r^o = -3.477/T_r + 3.555$, and the azeotropic lines of the mixtures, (α) methanol (1) + ethyl methanoate (2) and (β) methanol (1) + ethyl ethanoate (2). (b) Plot of $\log p_r^o$ vs x_1 for the azeotropic lines of (α) methanol (1) + ethyl methanoate (2) and (β) methanol (1) + ethyl ethanoate (2).

(1971), by 33% from those of Akita and Yoshida (1963), and by 90% from those reported by Nikam et al. (1966), which were nearly twice our values. The discrepancies with respect to the cases published in the literature may be attributable to differences in the methods used to effect the density measurements, since these other workers used pycnometry instead of the vibrating-tube densimeters now in use at our laboratory. All the V_m^E values were negative, indicative of the existence of specific molecular clumping resulting in levels of contraction that decreased progressively as ester chain length increased. The high negative V_m^E values for methanol + ethyl methanoate indicate relevant associative effects, possibly due to formation of complexes methanol + ester, which decrease with the increases of the ester chain.

Table 5. Coefficients A, B, C and Standard Deviation, $s(p_i^0)$ Obtained for Antoine Equation, $\log[p_i^0/(\text{kPa})] = A - B/[T(\text{K}) - C]$, and Others from Literature

compound	A	B	C	$\Delta T/\text{K}$	$s(p_i^0)$	ref
ethyl methanoate	6.395 25	1272.809	37.4789	300–345	0.08	this work
	6.078 98	1101.000	57.1700	235–360		TRC k-5520, 1969
	6.143 56	1130.590	54.1500	230–375		Reid et al., 1988
ethyl ethanoate	6.326 00	1317.703	45.0667	325–370	0.06	this work
	6.133 60	1195.130	60.6800	250–380		TRC k-5550, 1969
	6.139 45	1211.899	57.1500	250–400		Reid et al., 1988
ethyl propanoate	6.301 10	1368.907	53.4555	335–400	0.08	this work
	6.142 85	1274.700	64.1500	260–400		TRC k-5580, 1969
	6.143 96	1274.700	64.1600	260–400		Reid et al., 1988
ethyl butanoate	6.360 30	1493.891	51.1302	355–420	0.06	this work
	5.274 55	921.056	112.7700	275–440		TRC k-5610, 1976
	6.073 04	1358.299	60.1500	275–445		Reid et al., 1988
methanol	7.208 36	1580.790	33.9380	310–360	0.02	this work
	7.022 39	1474.080	44.0200	258–356		Reid et al., 1988
	7.189 71	1582.290	32.1650	315–360		Blanco and Ortega, 1996a

Vapor Pressures. The influence of the vapor pressures or their correlations on the calculation of the activity coefficient values is well-known. According to our experience with mixtures of esters and alkanols, the calculation of the γ_i values and the adimensional Gibbs energy function, G_m^E/RT , is rather sensitive in the regions of extremely high and low concentrations, where the curves clearly displayed maximum and minimum γ_i values produced not only by the mutual and complex association effects in the ester–alkanol systems but also by the effect of unsuitable correlations of $p_i^0 = \varphi(T)$ on the calculations. For that reason, it is appropriate to determine new (T , p_i^0) values for the components over the small interval of working temperatures, to improve the correlations and the effect of the correlations when processing the VLE values. Although Blanco and Ortega (1996a) recently published experimental values for methanol, new vapor pressure values were measured again in this study. The differences in the correlations of the values using the Antoine equation were minimal and corroborated the earlier measurements. All these values appear in Table 5, together with the values for the ethyl esters determined by nonlinear regression of the VLE data. Table 4 presents the experimental vapor pressure values for the ethyl esters. The differences between the literature curves and those in this study for the same temperature range were less than 1%, except in the case of ethyl butanoate, for which the differences with respect to the TRC values (TRC, k-5610, 1976) were nearly 4%. Figure 2a plots the vapor pressure values on reduced coordinates, permitting the corresponding correlations to determine the acentric factors for each component, which are shown in Table 1, and they will be used in later calculations. There was good agreement with the literature values and those calculated using the empirical relations proposed by Lee–Kesler, from Reid et al. (1988), p 23.

Vapor–Liquid Equilibrium Values. Table 6 sets out the experimental isobaric VLE values at a pressure of (141.3 ± 0.2) kPa for each of the binary methanol (1) + ethyl ester (2) systems. The values were calculated from the activity coefficients for the liquid phase using the expression

$$\gamma_i = \left(\frac{p y_i}{p_i^0 x_i} \right) \exp \left[\frac{(B_{ii} - V_i^0)(p - p_i^0)}{RT} \right] \exp \left[\frac{p}{2RT} \sum_j \sum_k y_j y_k (2\delta_{ji} - \delta_{jk}) \right] \quad (2)$$

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

The molar volumes, V_i^0 and the changes taking place with temperature were determined using Rackett's equa-

tion as modified by Spencer and Danner (1972) and the acentric factors, ω , to calculate the factor Z_{RA} by means of an empirical expression (see Reid et al. (1988)). The correlations proposed by Tsonopoulos (1974) were used to calculate the second virial coefficients for both the pure components and the mixtures. Table 6 shows the γ_i values and the adimensional Gibbs function, G_m^E/RT , for each concentration of methanol at equilibrium; the values are plotted in Figure 3a–d. Values of γ_2 smaller than unity were observed in the region of low alkanol concentrations. Recalculation using the new Antoine constants for the methanol determined in this study (Table 5) yielded slightly higher values, though the differences were minor, <1% in all the cases except for the ethyl butanoate, for which the values were 5% higher than the values given in Table 6. That difference was similar to the difference between the vapor pressure correlations and the literature values; that is, the influence of the new vapor pressure correlations in this study was minimal. The results suggest that the presence of the minimum and maximum γ_i values and the inflection in the Gibbs energy may have been a result of size and shape interactions in the methanol + ester systems, since these findings were made for the mixtures consisting of methanol and the esters with higher molecular weights (propanoate and butanoate), where size interactions occur on account of structural differences in the molecules, giving rise to an exothermic component in the mixing process. Furthermore, it is well-known that the autoassociation of methanol produces an endothermic effect in the mixture because of destruction of hydrogen bonds. That effect prevails on the contrary effect, exothermic, owing to formation of complexes or associated compounds between methanol–ester. In summary, the decrease in H_m^E values and the increase in the S_m^E values caused inflections in the G_m^E values, because $G_m^E = H_m^E - TS_m^E$.

The thermodynamic consistency of the experimental values given in Table 6 was verified using the point-to-point tests proposed by Fredenslund et al. (1977) and Wisniak (1993) and was positive in all the cases except for the Wisniak test applied to the mixture methanol (1) + ethyl methanoate (2). In the Fredenslund test the influence of the enthalpic term $(\Delta H_m^E/RT^2)(dT/dx_1)$ was practically negligible.

The literature has only published isobaric VLE studies for the mixture methanol (1) + ethyl ethanoate (2), though all the values have been determined at atmospheric or subatmospheric pressure; see Gmehling et al. (1996), Vol. 2a, pp 154–167, Vol. 2e, p 108. In order to clarify the comparison, we have only some of them. So, in the graphic representation of the magnitude $(y_1 - x_1)$ on x_1 in Figure 4

Table 6. VLE Experimental Values, T - x - y , and Calculated Obtained at 141.3 kPa for Binary Systems Methanol (1) + Ethyl Esters (2)

T/K	x_1	y_1	γ_1	γ_2	G_m^E/RT	T/K	x_1	y_1	γ_1	γ_2	G_m^E/RT
Methanol (1) + Ethyl Methanoate (2)											
337.45	0.000	0.000		1.000	0.000	335.93	0.699	0.521	1.084	1.660	0.209
337.15	0.017	0.044	3.485	0.978	0.001	336.51	0.743	0.552	1.058	1.786	0.191
336.80	0.033	0.075	3.216	0.972	0.011	337.30	0.783	0.588	1.038	1.894	0.169
336.25	0.061	0.117	2.784	0.971	0.034	337.96	0.812	0.620	1.029	1.982	0.152
335.54	0.094	0.158	2.479	0.982	0.069	338.43	0.834	0.648	1.029	2.049	0.143
335.05	0.120	0.187	2.339	0.992	0.095	339.36	0.864	0.688	1.019	2.150	0.121
334.37	0.174	0.236	2.098	1.013	0.140	340.51	0.888	0.735	1.014	2.144	0.098
333.99	0.224	0.275	1.928	1.036	0.174	341.33	0.911	0.773	1.009	2.268	0.081
333.80	0.290	0.318	1.727	1.073	0.208	342.32	0.932	0.816	1.004	2.321	0.062
333.75	0.336	0.338	1.590	1.114	0.228	343.30	0.953	0.862	1.002	2.430	0.044
333.85	0.416	0.376	1.422	1.191	0.249	344.34	0.973	0.913	1.000	2.605	0.026
334.20	0.496	0.409	1.282	1.291	0.252	345.04	0.985	0.949	1.003	2.621	0.017
334.70	0.583	0.450	1.176	1.431	0.244	345.50	0.993	0.977	1.006	2.693	0.013
335.19	0.647	0.482	1.115	1.566	0.229	345.92	1.000	1.000	1.000		0.000
Methanol (1) + Ethyl Ethanoate (2)											
360.62	0.000	0.000		1.000	0.000	344.65	0.516	0.636	1.300	1.222	0.232
358.69	0.020	0.078	2.579	0.995	0.013	344.32	0.566	0.660	1.244	1.286	0.233
357.55	0.043	0.134	2.135	0.989	0.022	344.07	0.628	0.686	1.176	1.397	0.226
356.19	0.063	0.190	2.157	0.983	0.032	343.90	0.691	0.716	1.123	1.529	0.212
355.14	0.082	0.234	2.093	0.980	0.042	343.85	0.732	0.733	1.087	1.659	0.197
354.16	0.101	0.270	2.034	0.981	0.055	344.01	0.822	0.791	1.038	1.948	0.150
352.66	0.129	0.325	2.012	0.980	0.073	344.18	0.859	0.821	1.025	2.093	0.126
350.14	0.184	0.409	1.940	0.989	0.112	344.67	0.920	0.881	1.010	2.397	0.080
348.66	0.233	0.465	1.828	0.998	0.139	344.95	0.942	0.907	1.004	2.587	0.059
347.51	0.285	0.506	1.689	1.026	0.168	345.21	0.961	0.930	1.000	2.899	0.041
346.74	0.331	0.536	1.586	1.054	0.188	345.58	0.975	0.949	0.993	3.269	0.022
346.05	0.371	0.565	1.527	1.075	0.203	345.88	0.991	0.981	0.999	3.369	0.010
345.68	0.411	0.579	1.433	1.124	0.217	345.92	1.000	1.000	1.000		0.000
345.02	0.464	0.612	1.373	1.161	0.227						
Methanol (1) + Ethyl Propanoate (2)											
383.24	0.000	0.000		1.000	0.000	353.85	0.349	0.720	1.580	1.043	0.187
379.01	0.025	0.134	1.870	0.998	0.014	352.95	0.385	0.740	1.516	1.057	0.195
375.19	0.052	0.252	1.900	0.988	0.022	351.40	0.445	0.767	1.434	1.106	0.217
372.72	0.072	0.323	1.904	0.980	0.028	349.85	0.548	0.797	1.278	1.245	0.234
370.90	0.086	0.373	1.929	0.974	0.033	348.46	0.664	0.828	1.149	1.488	0.226
368.45	0.106	0.432	1.957	0.970	0.044	347.54	0.750	0.851	1.080	1.789	0.203
366.49	0.125	0.478	1.943	0.968	0.054	347.07	0.805	0.879	1.057	1.893	0.169
365.04	0.140	0.513	1.960	0.958	0.057	346.70	0.861	0.906	1.032	2.088	0.129
362.67	0.170	0.561	1.898	0.965	0.079	346.45	0.896	0.923	1.020	2.291	0.104
361.68	0.183	0.580	1.883	0.966	0.088	346.20	0.926	0.945	1.018	2.354	0.080
360.22	0.206	0.604	1.824	0.982	0.110	346.04	0.970	0.973	1.007	2.814	0.038
358.28	0.243	0.644	1.751	0.987	0.126	346.00	0.983	0.985	1.007	2.776	0.024
357.21	0.265	0.662	1.709	0.998	0.141	345.92	1.000	1.000	1.000		0.000
355.75	0.298	0.687	1.658	1.015	0.161						
Methanol (1) + Ethyl Butanoate (2)											
405.90	0.000	0.000		1.000	0.000	351.75	0.578	0.891	1.269	1.349	0.264
403.75	0.009	0.065	1.266	0.999	0.001	350.45	0.667	0.908	1.171	1.514	0.243
397.13	0.033	0.241	1.568	0.990	0.006	349.73	0.724	0.919	1.120	1.657	0.221
392.09	0.051	0.354	1.713	0.986	0.014	348.96	0.785	0.932	1.075	1.847	0.189
386.67	0.076	0.470	1.754	0.971	0.015	348.13	0.849	0.946	1.040	2.125	0.147
382.45	0.095	0.545	1.833	0.962	0.022	347.64	0.882	0.958	1.029	2.206	0.118
376.55	0.131	0.634	1.818	0.966	0.048	347.35	0.908	0.962	1.016	2.505	0.099
371.75	0.162	0.692	1.855	0.978	0.081	346.98	0.932	0.970	1.010	2.795	0.079
367.57	0.199	0.742	1.833	0.983	0.107	346.66	0.956	0.979	1.005	3.088	0.054
362.65	0.260	0.789	1.744	1.021	0.160	346.39	0.974	0.987	1.005	3.154	0.035
359.05	0.330	0.827	1.617	1.046	0.188	346.25	0.982	0.990	1.005	3.407	0.027
355.75	0.386	0.853	1.589	1.092	0.233	345.92	1.000	1.000	1.000		0.000
353.07	0.501	0.879	1.381	1.213	0.258						

shows that the curves published by the various researchers have all been regular, increasing progressively with pressure, except for the values published by van Zandijcke and Verhoeve (1974), from Gmehling et al. (1996), Vol. 2a, p 167, at 101.3 kPa, which were not consistent and measured at higher than those at 141.3 kPa.

Azeotropes. Two of the binary systems considered in this study presented azeotropes at the working pressure of 141.3 kPa, methanol (1) + ethyl methanoate (2) at $x_1 = 0.337$ and $T = 333.7$ K, and methanol (1) + ethyl ethanoate (2) at $x_1 = 0.742$ and $T = 343.8$ K. The literature has reported numerous azeotropes for these mixtures (Gme-

hling et al., 1994), though they are not directly comparable because of differences in the experimental conditions. Figure 2a plots the azeotropic points from the literature and those recorded experimentally in this study employing the same system of representation used for the reduced vapor pressures for the pure components. To that end the corresponding geometric means of the individual values, i.e., $p_{cij} = (p_{ci}p_{cj})^{1/2}$ and $T_{cij} = (T_{ci}T_{cj})^{1/2}$, were used as the mixing rules for the critical pressure and temperature, respectively. Linear regression yielded the corresponding azeotropic lines for the methanol + ethyl methanoate, $\log p_r^c = -3.271/T_r + 3.328$, and for the methanol + ethyl

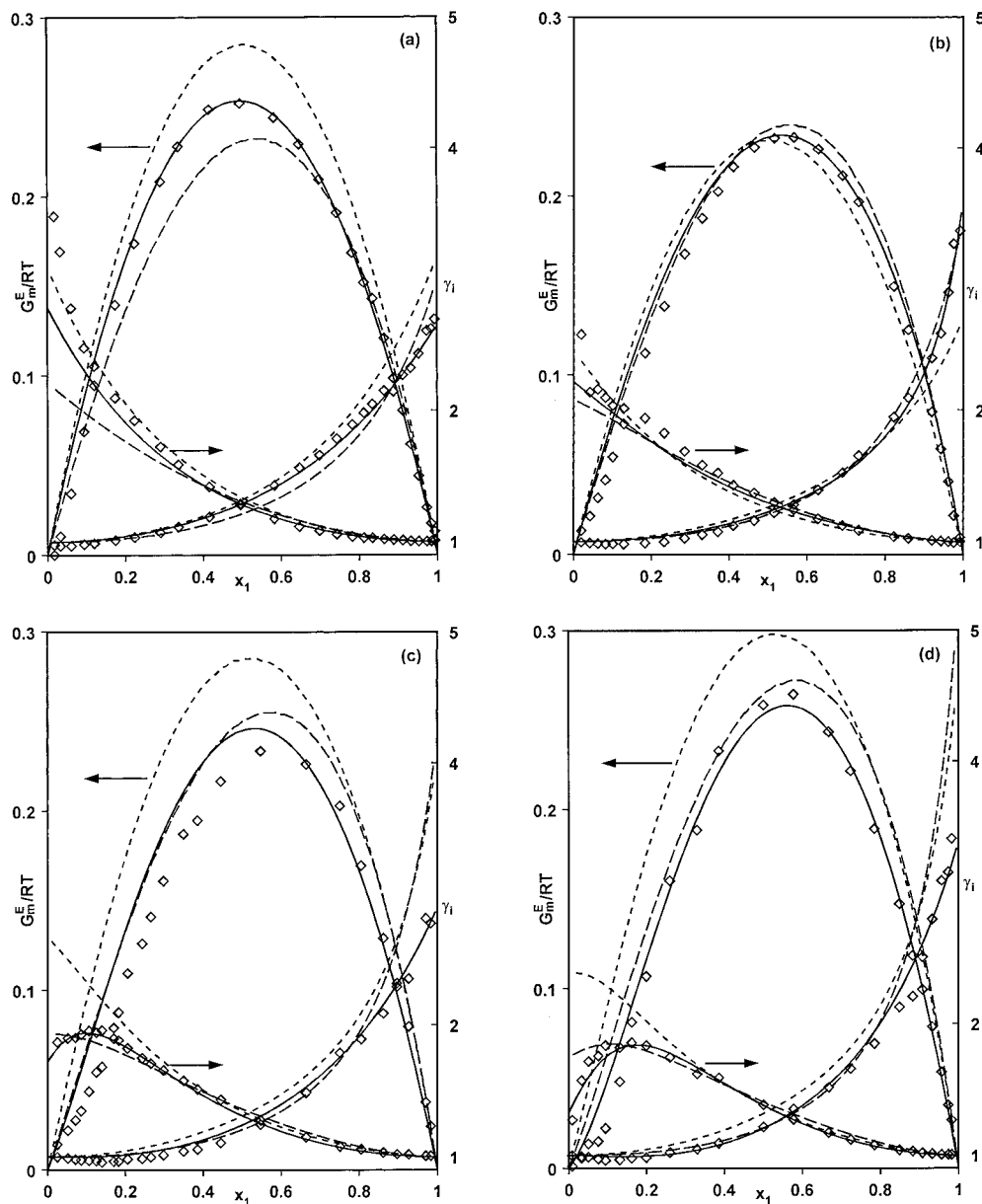


Figure 3. Experimental values (\diamond) and curves corresponding to G_m^E/RT and γ_i vs x_1 for the mixtures CH_3OH (1) + $\text{C}_{u-1}\text{H}_{2u-1}\text{CO}_2\text{C}_2\text{H}_5$ (2). (—) Fitting curves obtained by using of eq 5, and curves predicted by ASOG (---) and UNIFAC (Gmehling et al., 1993) (-.-).

ethanoate, $\log p_i^s = -3.739/T_r + 3.996$. Since in these calculations the mixtures were considered as homogeneous substances, the values for the acentric factors calculated here using the correlations obtained for these mixtures differed slightly from the values obtained using the arithmetic means of the factors for the pure components from Table 1, as expected on using geometric means for the critical magnitudes. Figure 2b depicts the correlations for the concentrations at the azeotropic points and shows certain discrepancies in the values of x_1 for the system methanol (1) + ethyl ethanoate (2) published by certain researchers. The values for the system methanol (1) + ethyl methanoate (2), on the other hand, showed good agreement.

Correlation of the VLE Values. Reduction of the experimental VLE values in this study was performed using the equation for correlating the adimensional function $Q = G_m^E/RT$ on x_1 put forward in previous papers. As before, a polynomial equation similar to eq 1 of the form

$$Q = x_1x_2(A_0 + A_1z + A_2z^2 + \dots) \quad (3)$$

where $z = x_1/(x_1 + kx_2)$ was used to correlate the function Q . In order to enhance the applicability of the equation to the VLE values, the coefficient A_i values may be made temperature-dependent (Van Ness and Abbott, 1982), since under isobaric conditions $Q = Q[x_1, T(x_1)]$. The relationship with the mixing enthalpy and temperature for pure liquids and mixtures with constant compositions is known and is given by

$$\frac{dQ}{dT} = -\frac{H_m^E}{RT^2} \quad \text{or} \quad \frac{H_m^E}{x_1x_2RT} = -T \left[\frac{d(G_m^E/x_1x_2RT)}{dT} \right]_{p,x} \quad (4)$$

Bearing in mind that the enthalpy varies linearly with temperature, $H_m^E = a + bT$, hence, in accordance with eq 4, $G_m^E/RT = aT - b \ln T + c$, where c is another integration constant. The values of the parameters a , b , and c can be obtained from the regressions of H_m^E and G_m^E/RT on temperature, T , calculations which are not easy to perform for the mixtures considered using currently available literature values. Therefore, we propose a simple

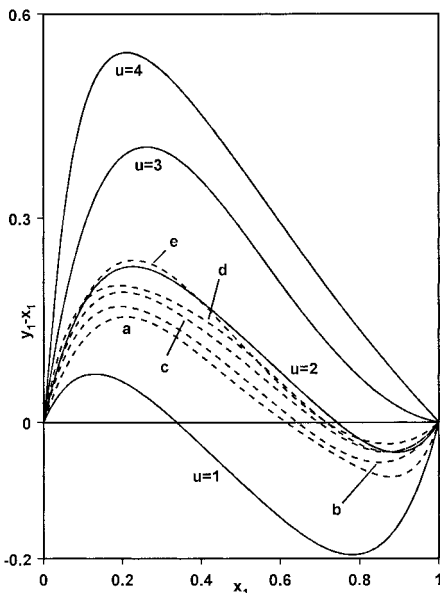


Figure 4. Representation of the correlation curves ($y_1 - x_1$) vs x_1 obtained for binary mixtures CH_3OH (1) + $\text{C}_{u-1}\text{H}_{2u-1}\text{CO}_2\text{C}_2\text{H}_5$ (2) in this work (solid lines), and those from literature (broken lines); (a, b, c) Park et al. (1973), from Gmehling et al. (1996), Vol. 2a, pp 164–166, at, respectively 13.3, 26.7, and 66.7 kPa; (d) Nagata (1962), from Gmehling et al. (1996), Vol. 2a, p 161, at 101.3 kPa; (e) van Zandijcke and Verhoeve (1974) from Gmehling et al. (1996), Vol. 2a, p 167, at 101.3 kPa.

Table 7. Coefficients of Eq 7 Obtained in Correlation of Experimental Excess Enthalpies, H_m^E/RT , vs x_1

mixture	k	A_0^1	A_1^1
methanol (1) + ethyl methanoate (2) ^a	0.302	2.172	-1.124
methanol (1) + ethyl ethanoate (2) ^b	1.992	2.081	-0.978
methanol (1) + ethyl propanoate (2) ^a	0.431	2.477	-1.169
methanol (1) + ethyl butanoate (2) ^a	0.344	2.223	-0.884

^a Ortega (1997). ^b Ortega (1995)

modification as a first approximation, namely, making the excess enthalpies temperature-independent. This is an excessively strict condition yielding $C_p^E = 0$, but it does permit simpler calculations when enthalpy values at different temperatures are not available. Obviously, the greater the difference between the temperature for which H_m^E values are available and the range of temperatures for the isobaric VLE values, the larger will be the errors arising from this assumption. In other words, if $H_m^E = A_{01}$ over the short temperature interval for the VLE measurements, then $C_m^E/T = A_{01}/T + A_{02}$. Thus, eq 3 is reduced to two terms and can be rewritten as

$$\frac{Q}{x_1 x_2} = \frac{G_m^E}{x_1 x_2 RT} = A_0 + A_1 z(k, x_1) \quad \text{where} \quad A_i = \frac{A_{i1}}{T} + A_{i2} \quad (5)$$

From eq 4 and the derivative of eq 5, we obtain

$$\frac{H_m^E}{x_1 x_2 RT} = -T \left(\frac{dA_0}{dT} \right)_x - T \left(\frac{dA_1}{dT} \right)_z - TA_1 \left(\frac{\partial z}{\partial k} \right) \left(\frac{dk}{dT} \right)_x \quad (6)$$

To simplify matters further, the parameter k can be also assumed to be temperature-independent, since that value only affects the shape of the fitted curve on concentration. Equation (6) can now be reduced to the first two terms and rewritten in a form similar to eq 5 as

$$H_m^E = x_1 x_2 RT (A_0^1 + A_1^1 z) \quad \text{where} \quad A_0^1 = -T \left(\frac{dA_0}{dT} \right)_x \quad \text{and} \\ A_1^1 = -T \left(\frac{dA_1}{dT} \right)_x \quad (7)$$

According to eq 5, the expressions relating the coefficients are given by $A_i^1 = A_{i1}/T$. In short, the constants in eq 5 are calculated using the H_m^E and G_m^E/RT values, which must be for the same or similar temperatures, as mentioned above. The most practical way to go about this is to determine the A_{i1} values by correlating the enthalpies, eq 7, and the A_{i2} values using the G_m^E/RT values for the VLE, eq 5. In our case, the enthalpy values nearest to equilibrium over the range of VLE temperatures, between 337 and 406 K, were those for the mixture methanol + ethyl methanoate at 318 K reported by Nagata et al. (1976). Since H_m^E values for the systems considered were unavailable over a range of temperatures, and since H_m^E was assumed to be temperature-independent, it was decided to use the H_m^E values measured at our laboratory at $T = 298.15$ K. Table 7 presents the coefficient values for the curves for $H_m^E = H_m^E(x_1)$ for the mixtures of methanol (1) + an ethyl ester (2) calculated in our study, equivalent to the A_{i1} values as per eq 7. The remaining coefficient, A_{i2} , values were calculated by simultaneously correlating the γ_i values and the Gibbs free energy function, G_m^E/RT , while minimizing the relations

$$\text{MCD} = \sum (\gamma_{1,\text{exp}} - \gamma_{1,\text{cal}})^2 + \sum (\gamma_{2,\text{exp}} - \gamma_{2,\text{cal}})^2 \quad (8)$$

$$\text{SD} = \left[\frac{\sum (Q_{\text{exp}} - Q_{\text{cal}})^2}{N - n} \right]^{1/2} \quad (9)$$

respectively, where N is the number of experimental values and n the number of coefficients used in the correlation. Table 8 sets out the coefficient values obtained as described

Table 8. Fitting Coefficients for Eq 5 Obtained Correlating the Magnitudes G_m^E/RT and γ_i vs x_1 and Standard Deviations $s(\gamma_i)$, $s(G_m^E/RT)$, and $s(H_m^E/RT)$

mixture	coefficients	$s(\gamma_i)$	$s(G_m^E/RT)$	$s(H_m^E/RT)$
methanol (1) + ethyl methanoate (2) eq 5	$k = 0.290$ $A_{01} = 593.28$ $A_{02} = -0.73$	0.119	0.010	2.5
methanol (1) + ethyl ethanoate (2) eq 5	$k = 5.625$ $A_{01} = 568.42$ $A_{02} = -0.78$	0.062	0.012	81.8
methanol (1) + ethyl propanoate (2) eq 5	$k = 0.256$ $A_{01} = 676.59$ $A_{02} = -1.22$	0.029	0.024	49.6
methanol (1) + ethyl butanoate (2) eq 5	$k = 0.365$ $A_{01} = 607.21$ $A_{02} = -1.22$	0.052	0.011	4.9

above for the correlations of the VLE data using eq 5 along with the standard deviations using eq 9 for γ_i , G_m^E/RT , and H_m^E for the mixtures. On the basis of the results, the differences in the enthalpy value estimates for the four mixtures considered were acceptable at less than 10%; hence, the proposed equation would appear to be appropriate for correlating isobaric VLE data for mixtures of methanol + an ethyl alkanoate.

Prediction of the VLE Values. Two versions of the UNIFAC group-contribution method and the ASOG model were used to predict the isobaric VLE values for the mixtures consisting of methanol (1) + an ethyl ester (2) studied. The interactions considered for the methanol/ester mixtures constitute one of the differences between these two models, the ASOG model using OH/COO, see Tochigi et al. (1990), for all alkanols and/or saturated esters; the UNIFAC model using a specific group, CH₃OH, for methanol, HCOO for the methanoates, and COOC for the other esters.

The models yielded generally acceptable estimates of the activity coefficient values, though there were some exceptions. The ASOG model provided good estimates for all the mixtures, with mean percentage differences of less than 7% for the γ_i values. The two versions of the UNIFAC model, Hansen et al. (1991) and Gmehling et al. (1993), yielded quite similar estimates, which were good for methanol + ethyl methanoate using the specific interaction for the methanoate, but the differences for the other mixtures increased progressively with ester chain length, attaining discrepancies on the order of 15%. The predictions made for non-methanoates with the modified version by Gmehling et al. (1993) showed prediction slightly better than by Hansen et al. (1991). Figures 3a–d present qualitative comparisons of the different estimates employing the ASOG and the version by Gmehling et al. (1993) of UNIFAC along with the curve obtained by eq 5 and clearly bear out the preceding comments.

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