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Isobaric Vapor–Liquid Equilibria and Excess Properties for the Binary Systems of Methyl Esters + Heptane

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The behavior was investigated for several binary mixtures that were composed of five methyl esters (from methanoate to pentanoate) with *n*-heptane, by using different thermodynamic quantities as obtained from experimental results such as isobaric vapor–liquid equilibria at the pressure 101.32 kPa and the corresponding excess properties. The equilibrium data show that all the mixtures reveal a positive deviation from ideality and that they are consistent with a point-to-point test. All the mixtures studied, with the exception of methyl pentanoate + *n*-heptane, reveal an azeotrope. Various equations were used to treat the equilibrium data. The use of a new polynomial correlation with temperature-dependent coefficients was deemed to be convenient. Various theoretical models were used in this study, including UNIFAC and ASOG, but the Gmehling et al. version was found to be more acceptable when estimating excess enthalpies with differences of between (3 and 17)%.

Introduction

The interaction of a substance in a solution is usually analyzed by observing the experimental behavior of this substance with a second inert component. There are a large number of studies of this effect which deal specifically with mixtures with alkyl esters. However, the first step to be taken when studying the behavior of these substances in solution is to analyze real data that address the interaction of esters with alkanes. In the existing literature, we have found experimental measurements of excess properties for this type of mixture. However, vapor–liquid equilibrium (VLE) data are scarce at either isobaric or isothermal conditions. Therefore, in this article our aim is to begin a systematic study of VLE for ester + alkane mixtures, beginning with the analysis of a set of binary mixtures of methyl esters (from methanoate to pentanoate) + *n*-heptane; the literature consists of isothermal data for just the mixture of methyl ethanoate + *n*-pentane.¹

In this study, the isobaric VLE data are determined at the pressure 101.32 kPa for the five binary mixtures mentioned above, using the experimental results of the excess quantities, enthalpies H_m^E , and volumes V_m^E to complement the study of their behavior. The VLE data are correlated using the classic equations of Wilson, NRTL, and UNIQUAC, and the data will be compared with those of a polynomial equation with temperature-dependent coefficients.

The last stage involves the estimation of data with two versions of the UNIFAC^{2,3} model together with the ASOG⁴ model, to observe the usefulness of those models for the prediction of thermodynamic quantities of ester + alkane mixtures.

Experimental Section

Materials. All components, with the exception of the methyl methanoate from Aldrich, were supplied by Fluka. The substances were degassed by ultrasound and treated in a molecular sieve (Fluka, 0.3 nm) to eliminate all traces of moisture, prior to use. Finally, the purities as specified by the manufacturer were verified for each substance with an HP-6890 gas chromatograph with an FID. The results were >99.5 mass % quality for heptane and >99.0 mass % for the rest of the components. Some of the physical properties determined experimentally for the pure substances are presented in Table 1, together with the comparison of these values with others found in the literature.

Apparatus and Procedure. The experimental equipment used to measure the isobaric VLE data consisted of a small capacity equilibrium still, 60 mL, in which the two phases were refluxed. The concentrations were taken from the density curves as obtained using an Anton-Paar (model DMA-55) densimeter with an uncertainty of $\pm 0.02 \text{ kg}\cdot\text{m}^{-3}$. The temperature was measured using an ASL-F25 thermometer calibrated periodically according to the ITS-90 standard with an uncertainty of $\pm 10 \text{ mK}$. The pressure was kept constant via the regulation and measurement system of Desgranges and Huot (model PPC2) with an uncertainty of $\pm 0.02 \text{ kPa}$.

Once equilibrium had been reached, as can be observed in the experimentation due to the constancy of the temperature and pressure, the concentrations of the liquid and vapor phases were measured using the density–concentration curve patterns as obtained for each of the mixtures in the study. These curves were obtained via the fit by least-squares of the direct experimental values (x_1 , ρ), which can be validated by observing, in turn, the quality of the data

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Table 1. Experimental Physical Properties of Pure Substances and Those from the Literature

component	T_b /K		$\rho(298.15\text{ K})/\text{kg}\cdot\text{m}^{-3}$		n_D at 298.15 K	
	exp	lit.	exp	lit.	exp	lit.
methyl methanoate	304.79	304.90 ^{a,b}	966.18	965.85 ^a 966.40 ^b	1.3412	1.3415 ^{a,b}
methyl ethanoate	329.85	330.09 ^a 330.02 ^b	927.14	928.00 ^a 927.90 ^b	1.3589	1.3589 ^{a,b}
methyl propanoate	351.65	352.60 ^a	908.59	907.79 ^a	1.3745	1.3742 ^a
methyl butanoate	375.53	375.90 ^a	892.52	892.99 ^a	1.3852	1.3847 ^a
methyl pentanoate	400.55		884.58	884.50 ^c	1.3947	1.3948 ^c
<i>n</i> -heptane	371.35	371.57 ^{a,b} 371.58 ^a	679.30	679.46 ^b 681.13 ^a	1.3853	1.38511 ^{a,b}

^a Reference 5. ^b Reference 6. ^c Reference 7.**Table 2. Densities ρ , and Excess Molar Volumes V_m^E for Binary Systems of Methyl Ester (1) + *n*-Heptane (2) at 298.15 K**

x_1	ρ kg·m ⁻³	$10^3 V_m^E$ m ³ ·mol ⁻¹	x_1	ρ kg·m ⁻³	$10^3 V_m^E$ m ³ ·mol ⁻¹
Methyl Methanoate (1) + Heptane (2)					
0.0420	682.76	369	0.7799	837.80	1288
0.1206	689.96	957	0.8321	861.36	1059
0.2235	702.15	1498	0.8729	882.18	853
0.3614	723.34	1856	0.9110	904.19	628
0.4593	741.73	1928	0.9460	926.26	421
0.5364	759.27	1884	0.9736	945.92	209
0.6079	778.20	1776	0.9935	961.30	43
0.6651	795.64	1639			
Methyl Ethanoate (1) + Heptane (2)					
0.0676	686.77	404	0.6215	786.97	1216
0.1019	690.81	588	0.6765	802.41	1095
0.1594	698.12	847	0.7204	815.61	989
0.2497	710.82	1164	0.7841	836.35	822
0.3137	721.10	1293	0.8342	854.72	639
0.4011	736.76	1391	0.8837	873.99	471
0.4829	753.42	1395	0.9248	891.52	312
0.5498	768.76	1324	0.9632	908.98	165
Methyl Propanoate (1) + Heptane (2)					
0.0640	687.65	319	0.6351	795.65	872
0.1117	694.35	501	0.7017	812.90	776
0.1561	700.97	637	0.7543	827.61	662
0.2628	718.15	877	0.8136	845.12	530
0.3650	736.50	995	0.8664	861.73	397
0.4343	750.10	1021	0.9030	873.85	295
0.5113	766.46	997	0.9689	896.98	103
0.5683	779.43	950			
Methyl Butanoate (1) + Heptane (2)					
0.0337	684.36	119	0.5333	775.25	712
0.0689	689.75	238	0.6085	791.88	639
0.1020	694.93	340	0.6618	804.18	572
0.1531	703.25	461	0.7161	817.10	500
0.2487	719.60	634	0.7869	834.67	389
0.3261	733.58	730	0.8394	848.24	295
0.3824	744.29	760	0.8882	861.22	211
0.4586	759.50	759	0.9255	871.41	144
Methyl Pentanoate (1) + Heptane (2)					
0.0172	682.12	70	0.5619	786.14	460
0.0613	689.72	172	0.6310	800.74	421
0.1404	703.90	310	0.7038	816.52	362
0.2074	716.09	401	0.7607	828.99	323
0.2867	731.09	461	0.8392	846.84	227
0.3552	744.33	488	0.9149	864.20	147
0.4135	755.77	501	0.9531	873.23	89
0.4931	771.88	487	0.9836	880.67	21

of V_m^E versus x_1 , and then using the $\rho = \rho(x_1)$ in the reverse calculation, that is, since the densities of the samples are known quantities, determining the concentrations of both phases in equilibrium, which can be estimated with a degree of precision higher than ± 0.002 mole fraction units.

The mixing enthalpies H_m^E were determined isothermally at the temperature 298.15 K, using a MS80D model

Table 3. Excess Enthalpies H_m^E for Binary Systems of Methyl Methanoate (1) + *n*-Heptane (2) at 298.15 K

x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H_m^E/\text{J}\cdot\text{mol}^{-1}$
0.0673	513.9	0.5354	2284.7	0.8313	1520.1
0.1535	1123.3	0.5709	2281.9	0.8721	1267.1
0.2499	1687.7	0.6389	2180.8	0.9068	981.1
0.3332	2023.6	0.6745	2118.7	0.9426	655.9
0.4008	2176.5	0.7144	2003.2	0.9730	337.7
0.4555	2252.5	0.7527	1892.7		
0.5004	2285.2	0.7940	1723.6		

Setaram standard system, which is calibrated electrically and periodically checked using pattern mixtures, such as cyclohexane + *n*-hexane and benzene + *n*-heptadecane. The uncertainty for the experimental values was calculated to be 1% of the H_m^E .

Results and Discussion

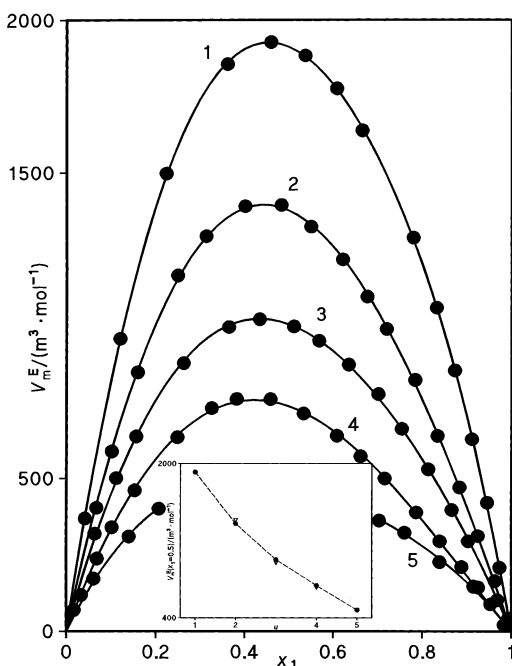
Excess Properties. For the mixtures considered, the excess properties $Y_m^E = V_m^E$ or H_m^E are obtained in this work. Table 2 gives the densities ρ and the excess volumes V_m^E , at various concentrations of ester for the five binary mixtures of methyl esters + *n*-heptane at the temperature 298.15 K. The pairs of values (x_1 , Y_m^E) were correlated using a polynomial equation of the type

$$Y_m^E = x_1 x_2 \sum_{j=0}^n b_j z^j \quad (1)$$

where, for volumes, $Y_m^E = 10^3 V_m^E/\text{m}^3\cdot\text{mol}^{-1}$ and $z = x_1/(x_1 + k_v x_2)$, where k_v is a constant value calculated as a quotient among the molar volumes of pure components at the working temperature $k_v = V_2^0/V_1^0$. In Table 4, we present the values as obtained for the b_j after the application of a procedure of least-squares and the corresponding standard deviations s , obtained for each of the mixtures. Figure 1 includes the experimental points and the corresponding fitting curves, with the regular decreasing variation of the equimolar excess volumes shown in the inset figure with the number of carbons atoms u of the acid portion of the methyl ester, $C_{u-1}H_{2u-1}COOCH_3$. The comparison with other data found in the literature⁸ for the same systems is satisfactory. The excess enthalpies, H_m^E , for the same mixtures, except for methyl methanoate + *n*-heptane, were published previously⁷ and will be used to the effects of this article to complete the study on VLE. For the binary mixture with methyl methanoate, the literature does not cover values measured at the temperature 298.15 K. Therefore, in Table 3, the measurements of H_m^E are given, as obtained experimentally for the mixture methyl methanoate + heptane and which were also correlated to eq 1, but where the value k , identified here as k_h , is determined by trial and error. Table 4 gives the values of the coef-

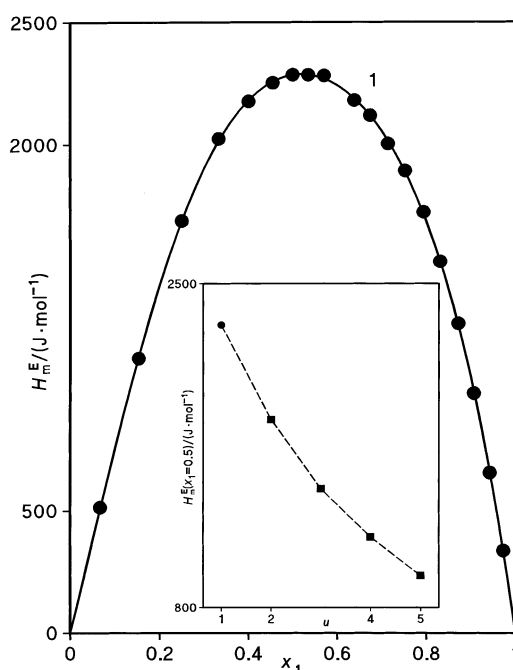
Table 4. Coefficients and Standard Deviation s Obtained Using Eq 1 To Correlate the Excess Properties V_m^E and H_m^E/RT

$V_m^E = 10^9 V_m^E$ in $\text{m}^3 \cdot \text{mol}^{-1}$						
binary mixture	k_v	b_0	b_1	b_2	$\frac{10^9 s(V_m^E)}{\text{m}^3 \cdot \text{mol}^{-1}}$	
<i>n</i> -heptane (2) +						
methyl methanoate (1)	2.373	9537	−10254	−5822	7	
methyl ethanoate (1)	1.846	6752	−4182	1815	8	
methyl propanoate (1)	1.521	5235	−3924	2146	7	
methyl butanoate (1)	1.289	3857	−2090		6	
methyl pentanoate (1)	1.123	2993	−3287	2174	8	
$Y_m^E = H_m^E/RT$						
binary mixture	k_h	b_0	b_1	b_2	b_3	$10^3 s(Y_m^E)$
<i>n</i> -heptane (2) +						
methyl methanoate (1) ^a	0.800	2.926	4.968	−11.322	8.721	3.2
methyl ethanoate (1) ^b	2.149	2.659	0.685			4.3
methyl propanoate (1) ^b	2.000	2.287	0.027			2.5
methyl butanoate (1) ^b	0.753	2.023	−0.239			1.5
methyl pentanoate (1) ^b	0.707	1.764	−0.346			2.1

^a This work. ^b Reference 7.**Figure 1.** Experimental (●) excess molar volumes V_m^E and correlation curves obtained at 298.15 K for the binary mixtures of $C_{u-1}H_{2u-1}COOCH_3$ (1) + $n\text{-C}_7\text{H}_{16}$ (2); labels indicate the u -values. The inset figure shows the variation of equimolar excess volumes of methyl esters + n -heptane mixtures as a function of the methyl ester chain length: (▽) values from the literature.⁸

ficients and standard deviations obtained in fitting the nondimensional function H_m^E/RT versus x_1 , which are identical to those of eq 4, whereas in Figure 2 we give the data and the correlation curve together with the regular variation in the equimolar enthalpies for methyl esters + n -heptane mixtures with the ester chain length u . The decrease in both quantities, V_m^E and H_m^E , with the increase in the number of groups $-\text{CH}_2-$ of the acid portion of the ester is due to the corresponding decrease in the dipolar moments of the methyl ester and the consequent decreasing of the dipole–dipole interactions.^{7,9}

Vapor Pressures. In the treatment of the VLE data, it is important to use precise data/correlations for vapor pressures. To that effect, in Table 6 we present the values of the Antoine constants for n -heptane and methyl esters.

**Figure 2.** Experimental (●) excess molar enthalpies H_m^E and correlation curve obtained at 298.15 K for the binary mixtures of HCOOCH_3 (1) + $n\text{-C}_7\text{H}_{16}$ (2). The inset figure shows the variation of equimolar excess enthalpies of methyl esters + n -heptane mixtures as a function of the methyl ester chain length: (■) values from the literature.⁷

For most of the pure substances in this article, we have obtained measurements previously. However, since the literature does not offer recent data for methyl pentanoate, measurements were carried out for (T, p°) using the same equilibrium ebulliometer. These values are presented in Table 5, and they were likewise correlated with the Antoine equation using a least-squares procedure; the constants are given in Table 6 together with those of the other substances used in this experiment. The values of the acentric factors ω for each component which appears in Table 6 were calculated using the Pitzer definition and are those used in the VLE data treatment.

In Figure 3, the lines of vapor pressure found using an analogous equation to Antoine's and using the Antoine constants and the critical temperature in accordance with

Table 5. Experimental Vapor Pressures p_i° for Methyl Pentanoate versus Temperature T

TK	p_i°/kPa	TK	p_i°/kPa	TK	p_i°/kPa	TK	p_i°/kPa
364.75	32.01	385.95	65.33	399.59	98.66	409.98	132.01
365.85	33.33	386.57	66.66	400.07	99.99	410.35	133.34
366.98	34.67	387.18	67.99	400.54	101.32	410.71	134.64
368.03	36.00	387.84	69.32	401.00	102.66	411.07	135.99
369.05	37.33	388.44	70.66	401.45	104.01	411.44	137.33
370.10	38.66	389.08	71.99	401.91	105.33	411.80	138.63
371.03	40.01	389.65	73.33	402.30	106.66	412.15	139.99
371.97	41.33	390.24	74.65	402.75	107.99	412.49	141.33
372.92	42.66	390.82	76.00	403.20	109.32	412.85	142.67
373.81	43.99	391.39	77.30	403.62	110.58	413.21	143.99
374.70	45.33	391.94	78.66	404.06	111.98	413.55	145.32
375.56	46.64	392.50	79.99	404.45	113.30	413.89	146.65
376.40	48.01	393.04	81.33	404.88	114.66	414.22	148.00
377.18	49.33	393.61	82.66	405.31	115.99	414.55	149.34
378.01	50.64	394.12	83.98	405.71	117.32	414.91	150.65
378.82	51.98	394.65	85.33	406.12	118.69	415.23	151.99
379.59	53.33	395.16	86.66	406.52	119.98	415.57	153.32
380.33	54.67	395.69	88.00	406.91	121.36	415.87	154.61
381.10	56.00	396.20	89.33	407.30	122.64	416.21	155.97
381.82	57.33	396.70	90.67	407.70	124.00	416.55	157.29
382.51	58.67	397.18	91.98	408.08	125.32	416.87	158.66
383.29	59.99	397.67	93.35	408.49	126.67	417.18	159.97
383.95	61.33	398.20	94.67	408.85	127.99		
384.62	62.68	398.65	95.99	409.23	129.32		
385.25	63.99	399.15	97.32	409.62	130.64		

Table 6. Coefficients A , B , and C of the Antoine Equation^a Used in This Work, and the Acentric Factors Calculated for Each Compound

compound	A	B	C	ω	ref
methyl methanoate	6.471 74	1216.48	32.78	0.269	unpublished ^b
methyl ethanoate	6.493 40	1329.46	33.52	0.329	10
methyl propanoate	6.604 20	1478.55	30.07	0.378	11
methyl butanoate	6.303 60	1381.64	53.60	0.371	12
methyl pentanoate	6.231 75	1429.00	62.30	0.439	this work
<i>n</i> -heptane	6.104 57	1296.68	54.81	0.342	13

^a $\log(p_i^\circ/\text{kPa}) = A - B/[T(K) - C]$. ^b Personal communication.

the indications of Ortega et al.¹⁴ are presented in reduced coordinates. We can observe a regular distribution of the lines of methyl ester (from methanoate to pentanoate) with a tendency to convergence in the region of high pressures and temperatures.

Presentation of VLE Data. In Table 7 we show the values of temperature T and the concentrations of the liquid phase x_i and vapor phase y_i given when equilibrium conditions are reached at $p = 101.32$ kPa, for the five binary mixtures $C_{u-1}H_{2u-1}COOCH_3$ ($u = 1-5$) (1) + n - C_7H_{16} (2). Using these values, the activity coefficients of the liquid phase were calculated by considering the vapor phase as ideal via the equation

$$\ln \gamma_i =$$

$$\ln \frac{y_i p}{x_i p_i^\circ} + \frac{(B_{ii} - V_i^L)(p - p_i^\circ)}{RT} + \frac{p}{2RT} \sum_{j=1}^n \sum_{k=1}^n y_j y_k (2\delta_{ji} - \delta_{jk}) \quad (2)$$

where the values of δ_{ji} and δ_{jk} can be calculated from the generalized expression $\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii}$ and the second virial coefficients of the pure components are calculated using the equations as proposed by Tsonopoulos.¹⁵ The molar volumes for the pure components V_i^L in the liquid phase and at the equilibrium temperature were calculated using the Rackett equation as modified by Spencer and Danner,¹⁶ with the Z_{RA} coefficients as extracted by Reid et al.¹⁷ Table 7 shows the activity coefficients for the compo-

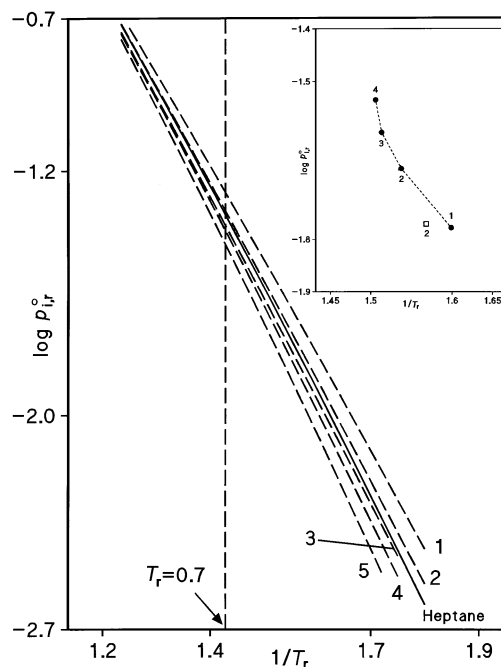


Figure 3. Vapor pressures lines in reduced coordinates for *n*-heptane (—) and methyl esters (---), $C_{u-1}H_{2u-1}COOCH_3$, calculated using the coefficients of Table 6. The inset figure shows the regular variation of the experimental azeotropes (●) with the methyl ester chain length and the values (□) found in the literature;¹⁹ labels indicate the u -values.

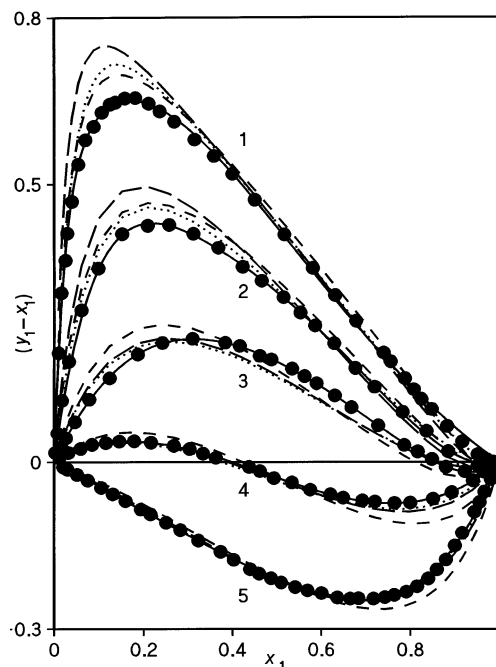


Figure 4. Experimental VLE values at 101.32 kPa and curves of $(y_1 - x_1)$ vs x_1 for the binary mixtures of $C_{u-1}H_{2u-1}COOCH_3$ (1) + n - C_7H_{16} (2) and the estimations made by ASOG⁴ (---), UNIFAC² (---), and modified-UNIFAC³ (···); labels indicate the u -values.

nents which constitute each mixture and the values corresponding to the nondimensional Gibbs function G_m^E/RT , for each equilibrium concentration. The values in Table 7 for the set of five binary systems were consistent with a point-to-point test as proposed by Fredenslund et al.¹⁸ In Figure 4, the $(y_1 - x_1)$ quantities are presented versus x_1 for the five mixtures in the study by considering the discrete values of Table 7 and the direct fitting curves using an equation similar to eq 1. These correlations and the

Table 7. Experimental and Calculated Values for the Isobaric VLE of the Binary Mixtures of Methyl Esters (1) + *n*-Heptane (2) at 101.3 kPa

<i>TK</i>	x_1	y_1	γ_1	γ_2	G_m^E/RT	<i>TK</i>	x_1	y_1	γ_1	γ_2	G_m^E/RT
Methyl Methanoate (1) + Heptane (2)											
363.95	0.0101	0.2062	3.688	0.988	0.001	308.70	0.4002	0.9186	2.023	1.271	0.426
358.95	0.0163	0.3208	3.984	0.990	0.013	307.90	0.4505	0.9227	1.857	1.364	0.450
355.79	0.0255	0.3882	3.338	0.994	0.024	307.39	0.5174	0.9269	1.654	1.505	0.458
353.00	0.0295	0.4414	3.505	0.996	0.033	306.95	0.5815	0.9303	1.500	1.687	0.455
349.38	0.0400	0.5091	3.275	0.996	0.043	306.65	0.6317	0.9319	1.399	1.899	0.448
344.78	0.0543	0.5899	3.153	0.986	0.049	306.47	0.6790	0.9328	1.311	2.167	0.432
340.75	0.0700	0.6498	3.007	0.985	0.063	305.82	0.7404	0.9369	1.236	2.594	0.404
337.55	0.0887	0.6925	2.765	0.989	0.080	306.07	0.7564	0.9370	1.199	2.727	0.382
334.15	0.1068	0.7362	2.689	0.980	0.088	305.73	0.7882	0.9387	1.167	3.101	0.361
331.20	0.1250	0.7690	2.617	0.979	0.102	305.55	0.8079	0.9388	1.146	3.443	0.348
329.22	0.1371	0.7845	2.583	0.998	0.129	305.65	0.8249	0.9383	1.118	3.792	0.325
325.99	0.1584	0.8131	2.558	1.006	0.154	305.37	0.8480	0.9432	1.104	4.070	0.297
322.96	0.1820	0.8375	2.520	1.016	0.181	305.17	0.8826	0.9476	1.074	4.906	0.249
320.20	0.2118	0.8573	2.421	1.035	0.214	305.01	0.9163	0.9531	1.046	6.209	0.194
318.18	0.2367	0.8680	2.342	1.075	0.257	304.79	0.9510	0.9649	1.029	8.025	0.129
315.55	0.2693	0.8821	2.282	1.120	0.305	304.71	0.9709	0.9755	1.022	9.460	0.086
312.80	0.3151	0.8956	2.173	1.191	0.364	304.68	0.9857	0.9864	1.018	10.753	0.052
310.30	0.3585	0.9095	2.114	1.230	0.401	304.69	0.9961	0.9957	1.017	12.272	0.027
Methyl Ethanoate (1) + Heptane (2)											
370.13	0.0024	0.0193	2.557	1.012	0.014	333.47	0.5155	0.8119	1.394	1.319	0.306
368.50	0.0075	0.0592	2.545	1.023	0.029	332.85	0.5538	0.8224	1.342	1.384	0.308
366.20	0.0196	0.1286	2.262	1.025	0.040	332.36	0.5866	0.8320	1.302	1.439	0.305
363.50	0.0362	0.2138	2.179	1.019	0.046	331.86	0.6295	0.8428	1.249	1.531	0.298
359.27	0.0672	0.3346	2.055	1.013	0.060	331.38	0.6770	0.8459	1.184	1.753	0.296
354.56	0.0989	0.4474	2.123	1.009	0.082	330.97	0.7200	0.8555	1.142	1.926	0.279
349.55	0.1523	0.5628	1.999	0.998	0.104	330.46	0.7830	0.8730	1.090	2.228	0.241
344.79	0.2098	0.6354	1.884	1.048	0.170	330.07	0.8361	0.8920	1.056	2.546	0.199
342.07	0.2579	0.6848	1.794	1.059	0.193	329.81	0.8846	0.9038	1.020	3.254	0.154
339.65	0.3124	0.7233	1.685	1.093	0.224	329.61	0.9510	0.9446	0.998	4.452	0.072
337.67	0.3687	0.7542	1.583	1.135	0.249	329.66	0.9805	0.9715	0.994	5.742	0.029
336.10	0.4235	0.7746	1.488	1.206	0.276	329.69	0.9935	0.9918	1.001	4.927	0.011
335.07	0.4664	0.7923	1.428	1.247	0.284						
Methyl Propanoate (1) + Heptane (2)											
370.26	0.0160	0.0428	1.547	0.998	0.005	352.28	0.5628	0.7173	1.248	1.145	0.184
369.67	0.0264	0.0695	1.547	0.997	0.009	351.96	0.5898	0.7315	1.227	1.171	0.185
368.57	0.0466	0.1188	1.544	0.995	0.016	351.57	0.6309	0.7506	1.191	1.224	0.185
366.90	0.0787	0.1914	1.544	0.992	0.026	351.25	0.6684	0.7668	1.160	1.288	0.183
364.71	0.1242	0.2752	1.497	0.997	0.048	350.83	0.7281	0.7939	1.117	1.407	0.174
361.98	0.1873	0.3808	1.486	0.996	0.071	350.58	0.7864	0.8168	1.073	1.606	0.156
359.85	0.2426	0.4568	1.465	1.000	0.093	350.54	0.8167	0.8355	1.058	1.682	0.141
357.60	0.3104	0.5322	1.427	1.014	0.120	350.60	0.8485	0.8539	1.039	1.805	0.122
355.58	0.3839	0.5985	1.379	1.038	0.146	350.62	0.8798	0.8712	1.021	2.004	0.102
354.81	0.4167	0.6255	1.359	1.048	0.155	350.75	0.9223	0.9058	1.009	2.258	0.071
353.88	0.4617	0.6525	1.317	1.086	0.171	351.24	0.9638	0.9468	0.994	2.695	0.030
353.40	0.4880	0.6721	1.303	1.094	0.175	351.42	0.9835	0.9735	0.995	2.929	0.013
352.66	0.5347	0.7025	1.271	1.118	0.180						
Methyl Butanoate (1) + Heptane (2)											
371.28	0.0137	0.0239	1.957	0.986	-0.004	368.24	0.4623	0.4462	1.185	1.120	0.139
370.95	0.0320	0.0488	1.728	0.989	0.006	368.32	0.4938	0.4648	1.153	1.147	0.140
370.50	0.0594	0.0835	1.614	0.993	0.022	368.47	0.5344	0.4977	1.135	1.166	0.139
370.08	0.0848	0.1159	1.589	0.996	0.036	368.68	0.5759	0.5262	1.107	1.200	0.136
369.73	0.1157	0.1501	1.524	1.001	0.050	368.98	0.6212	0.5634	1.088	1.227	0.130
369.39	0.1460	0.1831	1.488	1.006	0.063	369.21	0.6499	0.5858	1.074	1.252	0.125
369.07	0.1793	0.2168	1.449	1.013	0.077	369.62	0.6932	0.6242	1.060	1.281	0.116
368.76	0.2169	0.2519	1.405	1.023	0.092	369.93	0.7213	0.6503	1.051	1.301	0.109
368.46	0.2684	0.2976	1.353	1.037	0.108	370.49	0.7651	0.6916	1.036	1.340	0.096
368.36	0.3037	0.3271	1.318	1.047	0.116	371.01	0.8003	0.7273	1.025	1.373	0.083
368.25	0.3339	0.3489	1.283	1.062	0.124	371.90	0.8514	0.7855	1.013	1.416	0.063
368.23	0.3629	0.3706	1.255	1.074	0.128	372.75	0.8930	0.8387	1.006	1.445	0.044
368.20	0.4376	0.4290	1.205	1.105	0.138	373.89	0.9406	0.9077	0.999	1.443	0.021
Methyl Pentanoate (1) + Heptane (2)											
371.48	0.0204	0.0114	1.344	1.000	0.006	380.85	0.6009	0.3654	1.078	1.221	0.125
371.61	0.0300	0.0168	1.339	1.001	0.010	381.80	0.6363	0.3928	1.063	1.251	0.120
371.80	0.0515	0.0289	1.332	1.006	0.020	382.70	0.6654	0.4199	1.057	1.269	0.116
371.97	0.0755	0.0425	1.329	1.012	0.033	383.35	0.6842	0.4391	1.053	1.278	0.113
372.21	0.1056	0.0595	1.320	1.021	0.048	384.37	0.7177	0.4721	1.046	1.311	0.109
372.50	0.1315	0.0739	1.304	1.027	0.058	385.40	0.7432	0.5002	1.038	1.329	0.101
372.81	0.1600	0.0901	1.293	1.034	0.069	386.20	0.7643	0.5254	1.035	1.347	0.096
373.17	0.1947	0.1097	1.278	1.045	0.083	387.42	0.7912	0.5580	1.023	1.374	0.084
373.48	0.2162	0.1221	1.268	1.050	0.089	388.50	0.8152	0.5917	1.020	1.395	0.078
373.95	0.2512	0.1421	1.251	1.060	0.100	389.65	0.8402	0.6307	1.020	1.418	0.072
374.42	0.2833	0.1609	1.237	1.069	0.108	390.65	0.8596	0.6667	1.023	1.422	0.069
375.00	0.3239	0.1827	1.205	1.086	0.117	391.75	0.8800	0.7050	1.023	1.433	0.063
375.90	0.3739	0.2127	1.181	1.103	0.123	393.20	0.9000	0.7500	1.021	1.407	0.053
376.32	0.4034	0.2279	1.156	1.122	0.127	394.40	0.9158	0.7892	1.020	1.368	0.045
376.92	0.4403	0.2479	1.130	1.146	0.130	395.35	0.9303	0.8255	1.022	1.338	0.041
377.35	0.4604	0.2597	1.118	1.157	0.130	396.15	0.9437	0.8542	1.020	1.359	0.036
377.95	0.4874	0.2787	1.111	1.167	0.131	396.90	0.9555	0.8836	1.020	1.349	0.032
378.45	0.5103	0.2936	1.101	1.181	0.130	397.68	0.9662	0.9129	1.020	1.305	0.028
379.20	0.5417	0.3170	1.093	1.196	0.130	398.91	0.9809	0.9505	1.011	1.274	0.015
379.95	0.5694	0.3386	1.085	1.208	0.128	399.54	0.9894	0.9729	1.008	1.242	0.010

Table 8. Comparison between the Azeotropes Obtained Experimentally and Those Estimated by Several Theoretical Models and from the Literature for the Binary Mixtures Methyl Esters (1) + *n*-Heptane at 101.32 kPa

binary mixture	T_{az}/K	$x_{1,az}$	ref
methyl methanoate (1) + <i>n</i> -heptane (2)	304.69	0.992	this work
	304.76	0.946	UNIFAC ²
	305.13	0.946	UNIFAC ³
	304.25	0.940	ASOG ⁴
methyl ethanoate (1) + <i>n</i> -heptane (2)	329.60	0.934	this work
	329.75	0.973	Gmehling et al. ¹⁹
	329.09	0.909	UNIFAC ²
	329.70	0.968	UNIFAC ³
	329.33	0.936	ASOG ⁴
methyl propanoate (1) + <i>n</i> -heptane (2)	350.61	0.861	this work
	<352.75	<0.929	Gmehling et al. ¹⁹
	351.02	0.865	UNIFAC ²
	351.18	0.878	UNIFAC ³
methyl butanoate (1) + <i>n</i> -heptane (2)	350.00	0.812	ASOG ⁴
	368.22	0.398	this work
	368.25	0.346	Gmehling et al. ¹⁹
	368.08	0.389	UNIFAC ²
	375.29	0.375	UNIFAC ³
	368.20	0.424	ASOG ⁴

conditions of $(y_1 - x_1) = 0$ and $(dT/dx_1)_p = 0$ allowed us to determine the azeotropic points observed for each mixture, the values of which are represented in Table 8 together with those found in the literature.¹⁹ No azeotrope was found for the methyl pentanoate mixture. However, the azeotropes for the other three mixtures (ethanoate to butanoate) are largely uncertain, since they correspond, in the main, to the predictions of Lecat.¹⁹ The azeotropes in Table 8 are also plotted in Figure 3 using reduced coordi-

nates and considering the geometric mean of the critical properties of the pure substances as mixing rules to calculate the corresponding pseudocritical quantities. This graph shows a regular distribution of the values by considering the number of groups $-CH_2-$ in the methyl ester acid chain u .

Correlation and Prediction of VLE Data. The isobaric VLE data shown in Table 7 for each mixture were correlated using the models of local composition previously established in the field of equilibrium thermodynamics, such as those of Wilson, NRTL, and UNIQUAC. The values for the coefficients of these equations and the quality of each of the fits are to be seen in Table 9. Said correlations will serve by way of comparison and reference vis à vis the results obtained using another equation which is a modification of eq 1 by making the coefficients b_i depend on the temperature. The equations used are as follows:

$$\frac{G_m^E}{RT} = x_1 x_2 \left[\left(\frac{A_{01}}{T} + A_{02} \right) + \left(\frac{A_{11}}{T} + A_{12} \right) z + \left(\frac{A_{21}}{T} + A_{22} \right) z^2 \right] \quad (3)$$

where $z = x_1/(x_1 + k_g x_2)$

$$H_m^E/(RTx_1x_2) = \sum A_i^1 z^i \quad (4)$$

However, since $H_m^E = \left[\partial(G_m^E/RT)/\partial(1/T) \right]_{p,x}$, then the coefficients

$$A_{ji} = A_i^1 T \quad (5)$$

The correlation procedure followed with these equations uses the enthalpies fit as a starting point. Thus, with the

Table 9. Parameters for Different Equations Used in Correlation of VLE Data, and Standard Deviations s Obtained for Activity Coefficients γ_i , Nondimensional Gibbs Functions G_m^E/RT , and Excess Enthalpies H_m^E/R

equation	parameters	$s(\gamma_i)$	$s(G_m^E/RT)$	$s(H_m^E/R)$
(x ₁)Methyl Methanoate + (x ₂) <i>n</i> -Heptane				
Wilson	$\Delta\lambda_{12} = 3637.7^b$	$\Delta\lambda_{21} = 3371.5^b$	0.236	1209.9
NRTL, $\alpha = -0.80^a$	$\Delta g_{12} = 840.0^b$	$\Delta g_{21} = 2523.3^b$	0.153	714.4
UNIQUAC ($Z = 10$)	$\Delta u_{12} = 493.6^b$	$\Delta u_{21} = 1594.4^b$	0.165	844.0
eq 3, $k_g = 1.06$	$A_{01} = 1095.7$	$A_{11} = -1.771$	0.166	101.0
	$A_{02} = -15.3$	$A_{12} = -1.173$		
	$A_{03} = 620.2$	$A_{13} = -2.447$		
(x ₁)Methyl Ethanoate + (x ₂) <i>n</i> -Heptane				
Wilson	$\Delta\lambda_{12} = 2339.9^b$	$\Delta\lambda_{21} = 2587.5^b$	0.144	847.5
NRTL, $\alpha = -0.18^a$	$\Delta g_{12} = -5077.4^b$	$\Delta g_{21} = 6440.5^b$	0.142	198.7
UNIQUAC ($Z = 10$)	$\Delta u_{12} = 604.9^b$	$\Delta u_{21} = 655.9^b$	0.141	571.1
eq 3, $k_g = 0.69$	$A_{01} = 1048.1$	$A_{11} = -1.855$	0.111	65.2
	$A_{02} = -808.5$	$A_{12} = -1.657$		
	$A_{03} = 721.8$	$A_{13} = -0.981$		
(x ₁)Methyl Propanoate + (x ₂) <i>n</i> -Heptane				
Wilson	$\Delta\lambda_{12} = 398.4^b$	$\Delta\lambda_{21} = 3199.7^b$	0.028	797.7
NRTL, $\alpha = -0.97^a$	$\Delta g_{12} = -1007.3^b$	$\Delta g_{21} = 2151.7^b$	0.015	465.8
UNIQUAC ($Z = 10$)	$\Delta u_{12} = 1802.7^b$	$\Delta u_{21} = -847.3^b$	0.021	879.2
eq 3, $k_g = 1.16$	$A_{01} = 683.1$	$A_{11} = -1.501$	0.049	20.8
	$A_{02} = 27.4$	$A_{12} = 0.580$		
(x ₁)Methyl Butanoate + (x ₂) <i>n</i> -Heptane				
Wilson	$\Delta\lambda_{12} = 3134.1^b$	$\Delta\lambda_{21} = -1142^b$	0.040	841.2
NRTL, $\alpha = -0.72^a$	$\Delta g_{12} = 1644.9^b$	$\Delta g_{21} = -428.8^b$	0.039	523.4
UNIQUAC ($Z = 10$)	$\Delta u_{12} = -1126.2^b$	$\Delta u_{21} = 1900.8^b$	0.039	924.8
eq 3, $k_g = 6.69$	$A_{01} = 623.7$	$A_{11} = -1.104$	0.033	78.8
	$A_{02} = -87.1$	$A_{12} = -0.018$		
(x ₁)Methyl Pentanoate + (x ₂) <i>n</i> -Heptane				
Wilson	$\Delta\lambda_{12} = 1495.0^b$	$\Delta\lambda_{21} = -227.2^b$	0.057	564.1
NRTL, $\alpha = -0.06^a$	$\Delta g_{12} = 2061.3^b$	$\Delta g_{21} = -882.0^b$	0.058	508.8
UNIQUAC ($Z = 10$)	$\Delta u_{12} = -59.2^b$	$\Delta u_{21} = 347.9^b$	0.056	480.0
eq 3, $k_g = 1.84$	$A_{01} = 526.8$	$A_{11} = -1.068$	0.059	37.7
	$A_{02} = -103.4$	$A_{12} = 1.071$		
	$A_{03} = 0.10$	$A_{23} = -0.826$		

^a Obtained by fit. ^b In J·mol⁻¹.

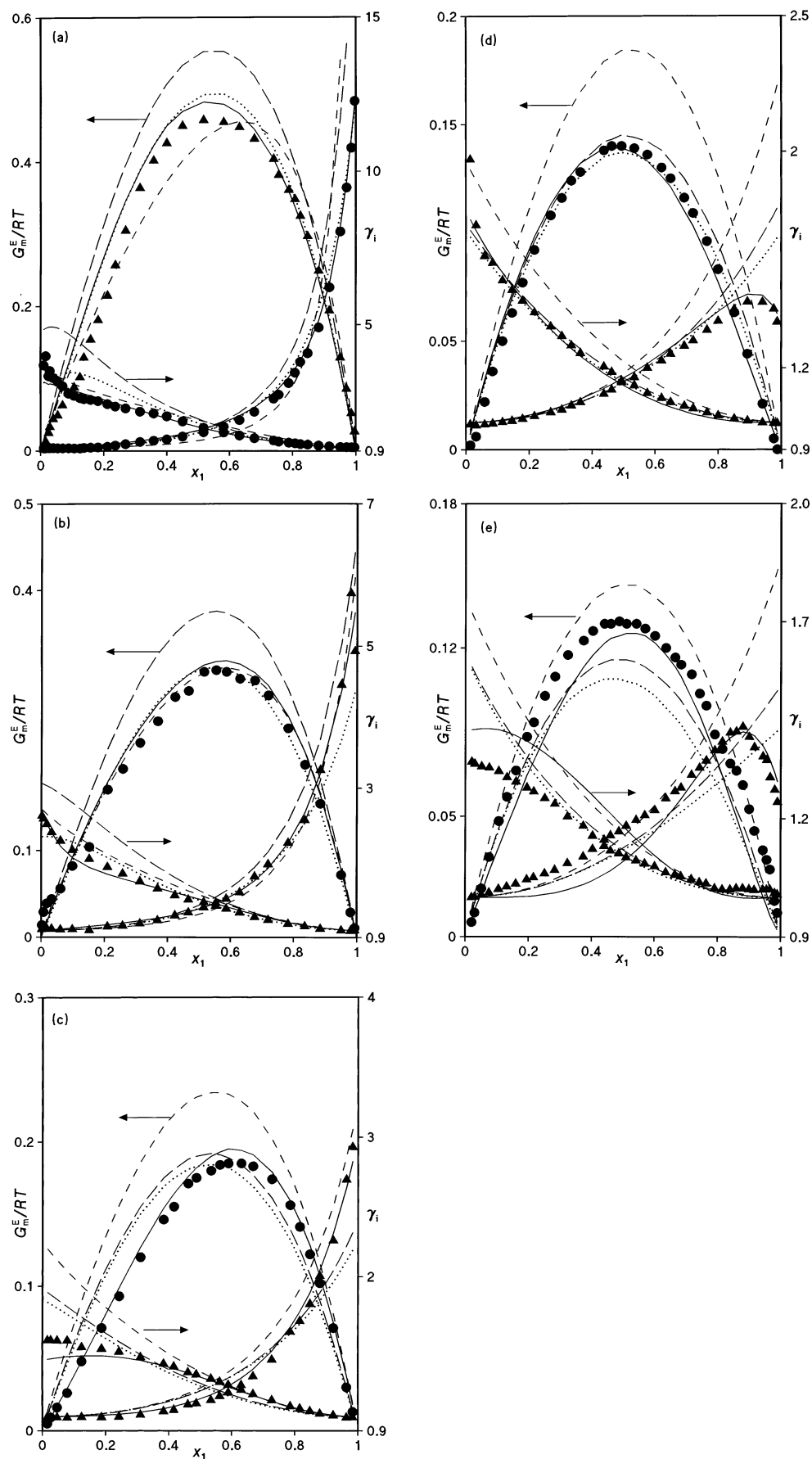


Figure 5. Experimental VLE values at 101.32 kPa. Fitted curve (—) and theoretical predictions of G_m^E/RT (\blacktriangle) and γ_i (\bullet) for the binary mixtures $C_{u-1}H_{2u-1}COOCH_3$ (1) + $n-C_7H_{16}$ (2): (a) for $u = 1$; (b) for $u = 2$; (c) for $u = 3$; (d) for $u = 4$; and (e) for $u = 5$; dashed curves represent the estimations by theoretical models: ASOG⁴ (---); UNIFAC² (— —); and modified-UNIFAC³ (···).

coefficients A_i^1 of eq 4, the sets of values for the same concentration of the nondimensional function of Gibbs and the activity coefficients for Table 7 are fitted, by now optimizing a new value of the parameter k , here called k_g , to attain a better correlation of the VLE quantities. This allows for the set of correlations obtained using eqs 3–5 to be acceptable, as is shown in the solid lines in Figure 5 for G_m^E/RT and γ_1 versus x_1 , thereby appreciating the excellent quality of the fits for each of the systems used. Table 9 shows the optimum values for the coefficients in eq 3, $A_{0,i}$, and the standard deviations for each of the quantities treated with an algorithm belonging to the computational subroutine Solver for the Excel spreadsheet, version 5.0a, by Microsoft. Likewise, the errors in the final calculation of excess enthalpies H_m^E are acceptable, since they are, in all cases, under 10%. With other correlation equations, the errors are far superior. Therefore, eq 3 is used for the simultaneous representation of the Gibbs function and the activity coefficients in Figure 5.

The theoretical estimations of the isobaric VLE at the pressure 101.32 kPa were obtained for the five mixtures of methyl ester (1) + *n*-heptane (2), using various models, the applications of which are interesting here in order to allow for their updating. The models used were ASOG, with the parameters as proposed by Tochigi et al.,⁴ the original version of the UNIFAC model with the parameters as presented by Hansen et al.,² and the version of the same method as modified by Gmehling et al.,³ which also allowed the estimations of the enthalpies of the systems studied. In Table 8, the estimates for the VLE concentrations are shown for the various models, whereas, in Figure 5, we show the estimations corresponding to the Gibbs functions and the activity coefficients. The set proposed by Gmehling et al.³ offers the best estimate for the VLE values and produces differences in the enthalpies of 17% and values which are always lower⁹ than the experimental values, except in the case of the methyl ethanoate + heptane system, where the predicted values are slightly higher with a mean error of under 4%. The best estimate of the azeotropic points, over all the different models (see Table 8), was also obtained using the version of UNIFAC as modified by Gmehling et al.³

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