Excess Properties and Isobaric Vapor−Liquid Equilibria for Binary Mixtures of Methyl Esters + *tert*-Butanol

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This article presents the experimental values obtained for excess properties H_m^E and V_m^E at two temperatures and vapor−liquid equilibria at 101.32 kPa for a group of four binary mixtures composed of four methyl alkanoates (methanoate to butanoate) with *tert*-butyl alcohol. The application of a point-to-point test to the equilibria data showed that the systems studied were consistent. The binary mixture methyl propanoate + *tert*-butyl alcohol presents an azeotrope at $x_{az} = 0.726$ and $T = 350.43$ K. All data were correlated by using a new equation with temperature-dependent coefficients by adjusting the quantities of VLE and the H_m^E simultaneously and modifying for each case the number of adjustable parameters. A good correlation was obtained for all mixtures. Application of the UNIFAC model to mixtures with *tert*-butyl alcohol produced inaccurate predictions with the version of Hansen et al. and acceptable estimates with the version of Gmehling et al. None of the models gave good estimates of the VLE of the methyl methanoate + *tert*-butyl alcohol mixture.

Introduction

In previous work,[1] excess properties H_m^E and V_m^E and the isobaric vapor−liquid equilibria (VLE) were measured at 101.32 kPa as part of a wider working project on binary systems of alkyl esters with alkanols[2−4] of the mixtures formed by the first four ethyl esters (methanoate to butanoate) with 2-methylpropan-2-ol (*tert*-butyl alcohol). As a follow up to this work, with the aim of studying in depth the behavior of a tertiary alkanol in solution, data are presented here for the same excess properties and the VLE of four binary mixtures of this tertiary alkanol but with the first four methyl esters (methanoate to butanoate).

For this work, the excess molar volume and excess molar enthalpies have been determined at two different temperatures. The literature consulted does not provide data for VLE and excess properties of binary mixtures considered here.

Experimental data were treated with a new form of an equation used in a previous paper[1] and later extended.[5] The efficacy of this equation is studied to fit the VLE and H_m^E data simultaneously. Finally, for predictive purposes two versions of the group contribution model of UNIFAC is used[6,7] to determine its ability to estimate properties of the whole group of mixtures of alkyl esters with a tertiary alkanol, extending the analysis and conclusions presented previously.[1]

Experimental Section

Materials. The methyl esters and *tert*-butyl alcohol used in the experimental work were the ones with the highest purity marketed by Fluka. All of them were previously degassed with ultrasound and treated with 0.3-nm molecular sieves (Fluka) to eliminate any trace of moisture. The quality of the substances was also verified with a GC (model HP-6890) equipped with an FID, and the degree of final purity was obtained, recorded in Table 1 for all products, was established in accordance with the manufacturer's recommendations. Moreover, the quality of the substances was also studied by measuring the values of some physical properties such as the normal boiling point, $T_{b,i}^o$, and density measurements, ρ, and refraction indices, n_D, at two temperatures, 298.15 K and 318.15 K, except for *tert*-butyl alcohol, which presents a melting point of 298.81 K that is recognized in the literature.[9] For the *tert*-butyl alcohol mixtures, the properties were determined at 299.15 K instead of 298.15 K. At the previously indicated temperatures, the values measured for *tert*-butyl alcohol and the methyl esters almost coincided with those published in previous work[1,12] and have, therefore, not been recorded here. Hence, in Table 1 only the values measured at 318.15 K are recorded, and good agreement is obtained with those recorded in the literature.

Apparatus and Procedures. The experimental equipment used to determine the isobaric VLE consisted of a small device, of around 60 cm^3, that works dynamically with the recirculation of both phases. Pressure control that was kept constant at (101.32 ± 0.02) kPa was done with a controller/calibrator device manufactured by Desgranges et Huot (model PPC2) with the above specified uncertainty. The temperature at each equilibrium stage is measured with an ASL-F25 thermometer, regularly calibrated according to the ITS-90, which presents an uncertainty in the measurement of ±10 mK.

Concentrations of the vapor and liquid phases of the binary systems of methyl esters (1) + *tert*-butyl alcohol (2), after reaching equilibrium states at constant pressure and temperature, are determined from the reference curve of densities versus concentration, which was previously obtained with samples of known composition at temperatures of 299.15 K for the system of methyl methanoate (1) + *tert*-butyl alcohol (2) and 303.15 and 318.15 K for the other systems. The densities were measured by an Anton Paar densimeter (model DMA-60/602) whose uncertainty was estimated to be ±0.01 kg·m^{-3}. The correlations of $\rho = \rho(x_1)$

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Table 1. Normal Boiling Point and Physical Properties of Pure Substances *tert*-Butanol and Methyl Esters Obtained Experimentally at 318.15 K

		$T^{o}_{b,i}$/K		ρ(318.15 K)/kg·m^{-3}		n_D(318.15 K)	
compound	mass fraction	exptl	lit	exptl	lit	exptl	lit
tert-butanol	0.997	355.58	355.57^{a,d} 355.50^{b}	759.87	759.45^{a,d}	1.3741	
methyl methanoate	0.992	304.79	304.90^{b,c}	964.78^{f}	964.84^{d,f}	1.3402^{f}	
methyl ethanoate	0.995	329.86	330.02^{b}	900.19	899.35^{d} 900.10	1.3486	1.3490^{e}
methyl propanoate	0.991	351.65	352.60^{c}	884.30	883.70^{d}	1.3641	
methyl butanoate	0.993	375.24	375.90^{c,d}	870.24	870.85^{d}	1.3753	

[a] Reference 8. [b] Reference 9. [c] Reference 10. [d] Values obtained by interpolation from ref 11. [e] Reference 13. [f] Values measured at 299.15 K.

for each mixture were carried out by applying an appropriate equation that contains a weighting factor with a simple second-degree polynomial form. These relationships were validated by confirming the quality of the results of V^{E}_{m} versus x_1 at each T. In this way, the inverse calculation of the mixtures in equilibrium, known as densities of the condensed vapor and liquid phases, is done with an uncertainty of better than ±0.002 units of the ester molar fraction. For the (x_1, V^{E}_{m}) values, the imprecision in the calculations of ester molar fractions was $\pm 5 \times 10^{-5}$ and $\pm 2 \times 10^{-9}$ m^3·mol^{-1} for V^{E}_{m}.

The excess enthalpies H^{E}_{m} were determined isothermically at temperatures of 299.15 K and 318.15 K for the four mixtures considered, with the exception of methyl methanoate (1) + *tert*-butyl alcohol (2) whose H^{E}_{m} values were measured only at 299.15 K. The uncertainty in the temperature measured in a Calvet calorimeter (model MS80D) was ±0.01 K when calibrating the equipment electrically by a Joule effect and regularly at both temperatures. The uncertainty of the experimental results was found to be lower than 1% of the H^{E}_{m} and $\pm 2 \times 10^{-4}$ in the ester concentrations.

Results

Excess Properties. Table 2 shows the experimental data obtained for pairs (x_1, V^{E}_{m}) of binary mixtures of methyl alkanoates (1) + *tert*-butyl alcohol (2), determined at temperatures of 303.15 and 318.15 K except for the mixture methyl methanoate (1) + *tert*-butyl alcohol (2), which was measured only at 299.15 K to avoid the vaporization of methyl methanoate ($T^{o}_{b,i}$ = 304.79 K) on one hand and the solidification of *tert*-butyl alcohol ($T^{o}_{m,i}$ = 298.81 K) on the other. This explains why the enthalpies of the studied mixtures were measured at 299.15 K and 318.15 K. The pairs of experimental values (x_1, H^{E}_{m}) are compiled in Table 3. Both excess quantities, represented generically by Y^{E}_{m}, were correlated with the equation

$$Y^{E}_{m} = z_1 z_2 \sum_{i=0}^{2} b_i z_1^{i} = z_1(1 - z_1)(b_0 + b_1 z_1 + b_2 {z_1}^{2})$$

$$z_1 = \frac{x_1}{x_1 + k x_2} \qquad (1)$$

where z_1 and/or the complementary $z_2 = 1 - z_1$ can be considered to be the active fraction of one of the two compounds of the binary mixture in the corresponding excess property. To correlate the excess volumes, the parameter k is identified with $k_v = V°_2/V°_1$, where V^{o}_{i} represents the molar volumes of each pure component i of the mixture measured at the same working temperature. (See Ortega et al.[14]) As described previously by Ortega et al.,[13,15] similar results are obtained for k_v via the quotient of group volume parameters R_k by the sum $r_i = \sum_k \upsilon_k^{(i)} R_k$, where $\upsilon_k^{(i)}$ is an integer that corresponds to the number of type k groups in a molecule of component i. The R_k parameters are the van der Waals group values given by Bondi.[16] However, this empirical method does not include the structural changes of all types of compounds such as the regioisomers or the temperature changes. For these purposes, it is preferable to use real V^{o}_{i} data for pure compounds. The correlation of enthalpy data in Table 3 was done also by applying eq 1, thus establishing a k value, identified now with k_h calculated from a weighted value of the real volumes of the substances with the theoretical parameters of area and volume, as indicated in Ortega et al.[13,15]

$$k_h = \left(\frac{q_2}{q_1}\right)\left(\frac{V^{o}_{2}}{V^{o}_{1}}\right)^{2/3}\left(\frac{r_1}{r_2}\right)^{2/3} = k_v^{2/3}\left(\frac{q_2}{q_1}\right)\left(\frac{r_1}{r_2}\right)^{2/3} \qquad (2)$$

where the q_i parameters are obtained from the sum of the area group parameters Q_k through $q_i = \sum_k \upsilon_k^{(i)} Q_k$.

The values obtained for k_v and k_h with this procedure are recorded in the first numeric column of Table 4 for the set of four binary systems studied here. This Table also contains the estimates obtained for the coefficients b_i of eq 1, obtained with a least-squares procedure and the standard deviations $s(Y^{E}_{m})$ for each mixture. The experimental results and the fitting curves of (x_1, V^{E}_{m}) are represented in Figure 1 for three of the studied systems at 303.15 K, and the data corresponding to the methyl methanoate (1) + *tert*-butyl alcohol (2) mixture are shown at 299.15 K for the reason given previously. To avoid confusion, the values at 318.15 K are not represented on the same graph. The inset shows the change in equimolar volumes of V^{E}_{m} with the ester chain and temperature. From this, it can be deduced that $(\partial V^{E}_{m}/\partial T)_{p,x}$ is positive for mixtures of methyl ethanoate and methanoate and negative for the other two, methyl propanoate and butanoate with the tertiary alkanol.

In this way, Table 4 shows the coefficients obtained in the correlations of enthalpies and their standard deviations $s(H^{E}_{m})$, and Figure 2 presents the experimental values and the fitting curves of enthalpies at 299.15 K for the four mixtures (the measurements taken at 318.15 K have not been shown to avoid confusion), with the inset showing the change in excess equimolar enthalpies with temperature and the ester chain length. In this case, $(\partial H^{E}_{m}/\partial T)_{p,x}$ is negative for the set of systems studied.

For an in-depth analysis of the behavior of the ester + *iso*-alkanol mixtures, it is also advisable to have the results for other mixtures of a tertiary alcohol and other esters to compare them with those presented in other articles by our

Table 2. Excess Molar Volumes V_m^E for Binary Systems of Methyl Esters (1) + *tert*-Butanol (2) at Two Different Temperatures

x_1	$\frac{10^9 V_m^E}{m^3 \cdot mol^{-1}}$	x_1	$\frac{10^9 V_m^E}{m^3 \cdot mol^{-1}}$	x_1	$\frac{10^9 V_m^E}{m^3 \cdot mol^{-1}}$
T = 299.15 K					
Methyl Methanoate (1) + *tert*-Butyl Alcohol (2)					
0.0627	295	0.4033	1061	0.7382	834
0.1002	451	0.4976	1068	0.7939	746
0.1302	567	0.5076	1067	0.8111	704
0.1667	688	0.5726	1036	0.8902	501
0.2419	867	0.6163	994	0.9574	243
0.3190	988	0.6512	955		
0.3526	1025	0.7222	868		
T = 303.15 K					
Methyl Ethanoate (1) + *tert*-Butyl Alcohol (2)					
0.0451	165	0.3957	887	0.6956	742
0.0901	335	0.4411	904	0.7432	659
0.1537	506	0.4445	899	0.8016	554
0.1973	607	0.4964	892	0.8477	463
0.2481	702	0.5515	874	0.9067	328
0.2631	732	0.5677	868	0.9465	217
0.3042	809	0.5954	850		
0.3448	849	0.6467	794		
Methyl Propanoate (1) + *tert*-Butyl Alcohol (2)					
0.0517	152	0.4060	667	0.7520	491
0.1081	293	0.4603	678	0.8122	415
0.1525	388	0.5167	679	0.8545	348
0.2020	471	0.5558	668	0.9065	253
0.2516	543	0.6086	641	0.9394	173
0.3129	610	0.6546	607		
0.3638	648	0.7197	543		
Methyl Butanoate (1) + *tert*-Butyl Alcohol (2)					
0.0628	160	0.3916	630	0.7527	473
0.0928	236	0.4530	649	0.7928	420
0.1566	368	0.5059	651	0.8510	321
0.1940	430	0.5463	640	0.9115	206
0.2507	507	0.6022	617	0.9420	140
0.3088	569	0.6588	571		
0.3502	604	0.6980	537		
T = 318.15 K					
Methyl Ethanoate (1) + *tert*-Butyl Alcohol (2)					
0.1020	393	0.4596	941	0.7969	570
0.1650	561	0.5227	915	0.8256	531
0.2168	684	0.5784	891	0.9077	301
0.2804	771	0.6398	850	0.9496	186
0.3490	876	0.6786	806		
0.4031	916	0.7422	718		
Methyl Propanoate (1) + *tert*-Butyl Alcohol (2)					
0.0750	194	0.4165	639	0.7950	427
0.1476	315	0.4931	648	0.8267	368
0.1952	416	0.5472	641	0.8822	281
0.2636	498	0.6296	609	0.9493	139
0.3159	559	0.6429	587		
0.3628	606	0.7013	541		
Methyl Butanoate (1) + *tert*-Butyl Alcohol (2)					
0.1079	235	0.3257	554	0.5996	616
0.1326	291	0.3949	605	0.6675	574
0.1749	368	0.4521	630	0.7318	524
0.2201	434	0.4783	636	0.8163	404
0.2751	503	0.5500	631	0.8728	317

Table 3. Excess Molar Enthalpies H_m^E for Binary Systems of Methyl Esters (1) + *tert*-Butanol (2) at Two Different Temperatures

x_1	$\frac{H_m^E}{J \cdot mol^{-1}}$	x_1	$\frac{H_m^E}{J \cdot mol^{-1}}$	x_1	$\frac{H_m^E}{J \cdot mol^{-1}}$
T = 299.15 K					
Methyl Methanoate (1) + *tert*-Butyl Alcohol (2)					
0.0899	659.5	0.5567	2486.2	0.8206	1524.8
0.2020	1404.8	0.6017	2430.6	0.8697	1179.3
0.2873	1888.8	0.6287	2379.6	0.9187	778.1
0.3657	2209.1	0.6747	2250.8	0.9598	417.3
0.4323	2384.5	0.7222	2056.3		
0.5033	2485.6	0.7721	1811.0		
Methyl Ethanoate (1) + *tert*-Butyl Alcohol (2)					
0.0671	527.6	0.4675	2172.7	0.7293	1784.5
0.1369	996.6	0.4928	2186.1	0.7866	1538.6
0.2113	1426.6	0.5304	2194.1	0.8439	1222.1
0.2812	1745.7	0.5753	2162.1	0.9019	840.9
0.3492	1973.7	0.6226	2090.7	0.9551	446.8
0.4106	2107.7	0.6741	1964.4		
Methyl Propanoate (1) + *tert*-Butyl Alcohol (2)					
0.0603	419.5	0.4705	1939.4	0.7116	1619.4
0.1414	889.8	0.5159	1952.2	0.7778	1370.9
0.2285	1326.8	0.5343	1943.9	0.8496	1019.0
0.3164	1653.5	0.5899	1895.5	0.9351	481.5
0.3971	1851.1	0.6328	1820.5		
0.4573	1928.6	0.6447	1792.1		
Methyl Butanoate (1) + *tert*-Butyl Alcohol (2)					
0.0487	327.8	0.3915	1736.8	0.5745	1829.6
0.1046	659.8	0.4395	1802.1	0.6360	1743.7
0.1632	979.2	0.4853	1837.8	0.7063	1587.3
0.2233	1251.9	0.5221	1844.0	0.7780	1352.5
0.2830	1469.8	0.5268	1846.9	0.8552	1005.9
0.3383	1627.2	0.5545	1837.7	0.9325	539.9
T = 318.15 K					
Methyl Ethanoate (1) + *tert*-Butyl Alcohol (2)					
0.0710	472.3	0.4898	2050.3	0.7628	1535.7
0.1469	903.7	0.5407	2059.3	0.8170	1289.1
0.2304	1299.6	0.5865	2028.4	0.8636	1014.6
0.3022	1597.8	0.6105	1987.9	0.9085	726.4
0.3713	1816.7	0.6585	1886.9	0.9567	371.9
0.4322	1970.2	0.7110	1734.1		
Methyl Propanoate (1) + *tert*-Butyl Alcohol (2)					
0.0486	326.1	0.4076	1779.0	0.6986	1646.2
0.1007	639.1	0.4404	1838.0	0.7666	1405.4
0.1707	1003.4	0.4827	1861.9	0.8289	1138.0
0.2374	1298.6	0.5312	1883.1	0.8931	791.0
0.3021	1523.1	0.5820	1846.5	0.9582	391.3
0.3578	1674.7	0.6358	1768.8		
Methyl Butanoate (1) + *tert*-Butyl Alcohol (2)					
0.0458	292.0	0.3854	1677.1	0.6845	1625.0
0.1000	589.6	0.4221	1738.0	0.7505	1440.9
0.1556	865.3	0.4655	1785.5	0.8187	1171.4
0.2136	1145.3	0.5127	1803.9	0.8840	815.4
0.2734	1375.3	0.5632	1795.3	0.9472	425.7
0.3313	1546.5	0.6217	1739.7		

group[1–4] and to be able to make more generalized comments about these systems.

Vapor Pressures. Vapor pressures affect the values of the quantities that characterize the VLE. It is, therefore, usual in this kind of work to present experimental values for pairs (T, p_i^o) corresponding to the saturation curve of the pure compounds studied obtained with the same experimental equipment as the VLE. The vapor pressures of *tert*-butyl alcohol were presented in a previous article,[1] and those corresponding to three methyl esters (ethanoate to butanoate) were determined in our laboratory several years ago.[17–19] Therefore, we decided to make new measurements using the same equilibrium equipment but over a longer temperature interval and always with the restrictions of a glass ebullometer and to present, for the first time, the vapor pressures of methyl methanoate. The experimental results of T versus p_i^o for methyl esters are shown in Table 5 and are correlated with the well-known Antoine equation

$$\log(p_i^o/\text{kPa}) = A - \frac{B}{(T/\text{K}) - C} \tag{3}$$

where the constants A, B, and C are determined by a least-squares method (Table 6), comparing in this Table the values obtained with others from the literature that will be used to characterize the VLE of these mixtures. Figure 3 shows the vapor pressure lines of the compounds used

Table 4. Coefficients and Standard Deviation *s* Obtained Using Equation 1 to Correlate Excess Properties V_m^E and H_m^E

$Y_m^E = 10^9 V_m^E$ in ($m^3 \cdot mol^{-1}$)

binary mixture	k_v	b_o	b_1	b_2	$10^9 s(V_m^E)$ $m^3 \cdot mol^{-1}$
$T = 303.15$ K					
tert-butanol (2) +					
+ methyl methanoate (1)[a]	1.538	7918	−12 081	8516	6
+ methyl ethanoate (1)	1.197	5041	−4236	2403	13
+ methyl propanoate (1)	0.986	3207	−1711	1441	7
+ methyl butanoate (1)	0.835	2415	112	488	3
$T = 318.15$ K					
tert-butanol (2) +					
+ methyl ethanoate (1)	1.185	5079	−3796	1966	13
+ methyl propanoate (1)	0.979	2600	−156	270	8
+ methyl butanoate (1)	0.831	2189	87	1118	6

$Y_m^E = H_m^E$ in ($J \cdot mol^{-1}$)

binary mixture	k_h	b_0	b_1	b_2	$s(H_m^E)$ $J \cdot mol^{-1}$
$T = 299.15$ K					
tert-butanol (2) +					
+ methyl methanoate (1)	1.445	11 753.4	−2933.1	−1992.8	18.4
+ methyl ethanoate (1)	1.161	9915.6	−3145.1	1630.4	11.5
+ methyl propanoate (1)	0.974	7006.6	2001.3	−888.7	5.9
+ methyl butanoate (1)	0.840	6199.2	637.6	3025.7	13.3
$T = 318.15$ K					
tert-butanol (2) +					
+ methyl ethanoate (1)	1.153	7674.6	2318.2	−2594.6	13.7
+ methyl propanoate (1)	0.969	6840.6	588.3	1319.7	17.0
+ methyl butanoate (1)	0.833	5588.6	1794.5	2414.4	10.3

[a] At $T = 299.15$ K.

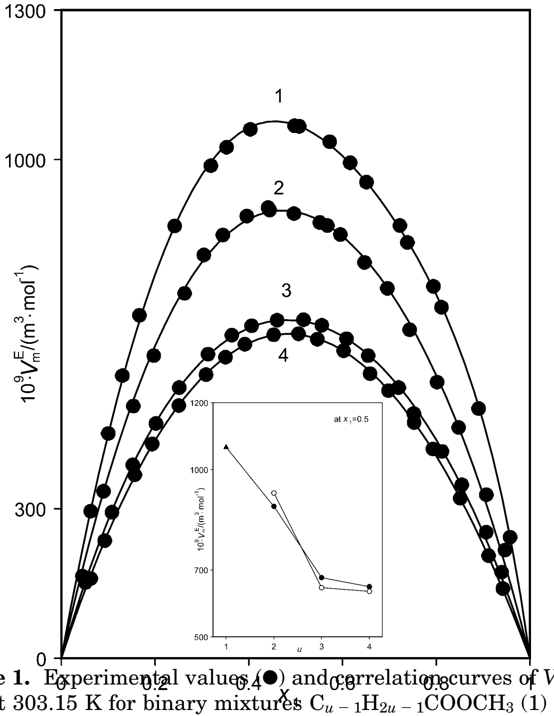

Figure 1. Experimental values (●) and correlation curves of V_m^E vs x_1 at 303.15 K for binary mixtures $C_{u-1}H_{2u-1}COOCH_3$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2); labels indicate the *u* values. The V_m^E for methyl methanoate ($u = 1$) + *tert*-butyl alcohol were measured at 299.15 K. The inset shows the variation of equimolar volumes as a function of *u* (▲) at 299.15 K for $u = 1$; (●) at 303.15 K for $u = 2, 3, 4$; and (○) at 318.15 K for $u = 2, 3, 4$.

in this work—methyl esters and *tert*-butyl alcohol—in reduced coordinates. Equations with reduced variables for each compound are determined from the values of the Antoine equation taking into account the analysis made by Ortega et al.[20]

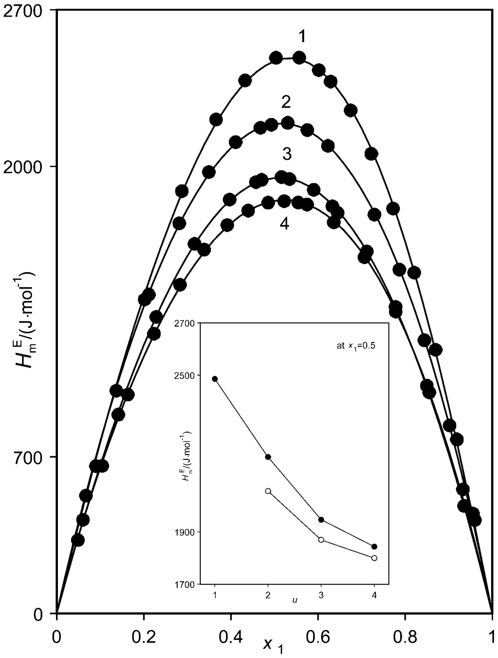

Figure 2. Experimental values (●) and correlation curves of H_m^E vs x_1 at 299.15 K for binary mixtures $C_{u-1}H_{2u-1}COOCH_3$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2); labels indicate the *u* values. The inset shows the variation of equimolar enthalpies as a function of *u* (●) at 299.15 K for $u = 1, 2, 3, 4$ and (○) at 318.15 K for $u = 2, 3, 4$.

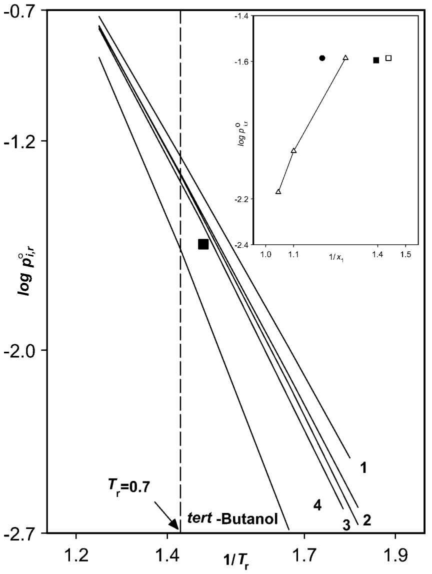

Figure 3. Vapor pressure lines in reduced coordinates for methyl esters $C_{u-1}H_{2u-1}$ $COOCH_3$ and *tert*-butanol calculated using the coefficients of Table 6 and the experimental azeotrope (!) for methyl propanoate (1) + *tert*-butyl alcohol (2); labels indicate the *u* values. The inset plots the situation of the azeotrope as a function of ester concentration and its comparison with the azeotropes found for mixtures with ethyl esters.[1]

$$\log p_{i,r}^o = \frac{B/T_c}{1 - (C/T_c)} - \frac{B/T_c}{T_r - (C/T_c)} \qquad (4)$$

The change from the original Antoine equation (eq 3) to eq 4 is achieved using the critical point of the pure

Table 5. Experimental Vapor Pressures p_i^o for Methyl Alkanoates

T/K	p_i^o/kPa	T/K	p_i^o/kPa	T/K	p_i^o/kPa	T/K	p_i^o/kPa	T/K	p_i^o/kPa	T/K	p_i^o/kPa
Methyl Methanoate											
301.23	88.70	306.20	106.72	310.64	125.47	314.37	143.32	316.57	154.75	319.37	170.00
301.42	89.37	306.54	108.06	310.92	126.77	314.60	144.13	316.71	155.22	319.45	170.76
301.78	90.67	306.84	109.39	311.19	128.14	314.63	144.65	316.95	156.54	319.67	171.98
302.15	91.98	307.20	110.77	311.48	129.44	314.88	145.45	317.05	157.42	319.93	173.32
302.53	93.31	307.54	112.13	311.78	130.75	314.93	145.65	317.17	157.73	320.22	174.76
302.89	94.64	307.85	113.44	312.06	132.09	315.12	146.74	317.36	158.92	320.34	175.82
303.41	95.98	308.13	114.75	312.37	133.48	315.18	147.03	317.40	159.14	320.65	177.38
303.77	97.36	308.47	116.10	312.67	134.81	315.52	148.79	317.64	160.45	320.78	178.57
304.13	98.69	308.81	117.47	312.90	136.09	315.56	149.41	317.88	161.72	321.04	180.01
304.44	99.97	309.15	118.77	313.17	137.42	315.77	150.23	318.00	162.65	321.34	181.70
304.79	101.32	309.43	120.12	313.45	138.75	316.00	151.48	318.34	164.18	321.46	182.37
304.83	101.39	309.72	121.43	313.74	139.83	316.06	152.08	318.51	165.32	321.72	184.02
305.21	102.89	310.03	122.74	314.01	141.42	316.23	152.97	318.68	166.44	321.94	185.46
305.51	104.06	310.33	124.08	314.30	142.78	316.47	154.04	319.07	168.30	322.20	186.83
305.85	105.38										
Methyl Ethanoate											
305.21	39.85	317.05	63.90	324.58	83.84	331.43	106.75	337.19	129.37	342.00	151.93
305.85	41.28	318.34	66.51	324.95	85.23	331.76	107.92	337.53	130.87	342.37	153.34
306.84	42.46	318.69	67.81	325.33	86.76	332.06	109.42	337.78	131.93	342.46	154.61
307.84	44.04	319.37	69.23	325.71	87.86	332.52	110.71	337.90	133.48	342.85	155.92
308.13	45.37	319.93	70.45	326.25	89.23	332.77	112.16	338.15	134.72	343.21	157.52
308.75	46.97	320.11	71.01	326.63	90.98	333.10	113.39	338.66	136.16	343.36	158.57
309.72	48.14	320.34	71.90	327.08	92.06	333.60	114.47	338.82	137.37	343.46	160.01
310.17	49.41	320.65	73.35	327.54	93.46	333.94	115.87	339.07	138.56	343.67	161.10
311.19	50.42	321.34	74.58	328.00	94.82	334.06	117.43	339.41	140.07	344.09	162.70
311.59	51.81	321.46	75.27	328.17	96.10	334.27	118.52	339.66	141.45	344.46	164.20
312.76	53.53	321.72	76.13	328.96	97.67	334.73	120.12	339.95	142.53	344.67	165.28
313.38	54.58	322.07	77.22	329.38	99.14	335.06	121.46	340.33	144.04	344.88	166.78
313.74	55.90	322.36	77.87	329.55	100.18	335.23	122.57	340.49	145.51	345.05	168.02
314.18	57.49	322.62	78.83	329.86	101.32	335.73	123.95	340.95	146.43	345.26	169.24
314.88	58.59	323.07	80.15	330.09	102.60	336.07	125.35	341.08	147.88	345.47	170.37
315.56	60.05	323.49	81.23	330.43	104.14	336.48	126.88	341.45	149.13	345.84	171.92
316.06	61.43	324.29	82.59	330.97	105.19	336.86	127.85	341.79	150.58	345.96	173.20
316.57	62.50										
Methyl Propanoate											
325.88	40.08	338.52	64.17	346.32	84.18	352.82	105.43	358.48	126.73	363.73	148.09
327.07	42.57	339.43	66.58	346.57	85.43	352.90	106.58	358.65	127.87	363.91	149.39
328.03	44.13	339.71	67.89	346.65	86.74	353.73	107.82	358.98	129.37	364.40	151.04
329.00	45.29	340.73	69.17	347.23	87.87	353.82	109.39	359.32	130.43	364.57	152.48
329.68	46.72	341.07	70.53	347.40	88.10	354.15	110.78	359.48	130.89	364.90	153.26
330.24	47.97	341.52	71.89	348.15	90.74	354.57	112.07	359.98	133.25	364.99	154.82
330.70	49.34	341.72	72.42	348.73	91.95	354.82	113.15	360.40	134.57	365.38	156.06
332.00	50.58	342.35	73.37	348.98	93.23	355.65	114.82	360.57	135.81	365.48	156.17
332.74	51.89	342.60	75.37	349.23	94.60	355.74	115.90	361.08	137.35	365.82	158.49
333.19	53.37	342.88	75.83	349.73	96.03	355.82	117.13	361.40	138.56	365.90	159.73
334.04	54.63	343.25	75.91	350.23	97.26	356.32	118.57	361.73	140.00	366.15	160.57
334.49	55.93	343.95	77.99	350.59	98.70	356.90	120.15	361.90	141.21	366.57	162.57
335.63	57.49	344.15	78.43	350.99	100.00	357.15	121.17	362.44	142.57	366.65	163.38
335.97	58.57	344.25	78.74	351.65	101.32	357.39	122.81	362.57	144.11	367.15	165.17
336.70	60.05	344.75	79.89	352.23	102.75	357.90	123.81	363.07	145.35	367.40	166.74
337.50	61.50	345.40	82.35	352.40	103.87	358.24	124.65	363.40	146.48	367.82	167.89
338.06	62.73	345.65	82.59								
Methyl Butanoate											
347.53	40.12	359.70	61.42	369.25	83.91	376.02	105.47	382.22	126.48	387.61	147.69
348.26	41.24	360.43	62.63	369.95	85.71	376.39	106.50	382.73	127.91	387.98	149.24
349.21	42.76	360.93	64.13	370.19	86.58	376.97	107.92	382.95	129.40	388.41	150.57
349.79	43.84	362.03	66.54	370.49	87.94	377.55	109.23	383.60	130.75	388.92	151.94
350.81	45.25	362.31	68.03	371.07	98.35	378.14	110.58	383.68	132.15	389.02	153.40
351.98	46.74	363.20	69.42	371.72	90.80	378.36	112.15	384.33	133.49	389.36	154.57
352.34	47.92	363.49	70.61	371.79	92.10	378.79	113.36	384.77	134.91	390.02	156.49
353.21	49.41	363.78	71.18	372.31	93.26	378.94	114.67	384.84	135.92	390.16	157.37
353.72	50.85	365.02	73.50	372.89	94.59	379.30	115.84	385.06	137.27	390.36	158.70
354.96	51.83	365.38	74.77	373.47	95.92	379.67	117.27	385.35	138.45	390.53	160.05
355.26	53.50	365.97	75.89	373.84	97.46	380.03	118.72	385.72	140.01	390.89	161.18
356.06	54.82	366.41	77.39	374.57	99.14	380.69	120.15	386.06	141.27	391.07	162.57
356.79	55.89	366.84	78.61	374.77	100.04	381.20	121.36	386.74	142.63	391.55	163.94
357.44	57.38	367.57	80.14	375.24	101.32	381.56	122.59	386.84	144.13	391.98	165.70
358.24	58.61	368.01	81.39	375.37	102.58	381.64	124.01	387.10	145.37	392.20	166.69
358.90	60.02	368.59	82.57	375.81	104.06	381.85	125.24	387.47	146.49		

substance as a boundary condition. However, because eq 3 is not applicable over such a wide range, the coefficients $a = b/(1 - c)$, $b = B/T_c$, and $c = C/T_c$ used to develop the reduced form of the Antoine equation can also be determined by direct fitting of the data (T_r, $p_{i,r}^o$). In this case, the values obtained for coefficients a, b, and c with both procedures were not very different. The acentric factors ω calculated for each of the substances (column 4 of Table 6), considering Pitzer's definition, presented acceptable agreement with those recorded in the literature. These

Table 6. Coefficients *A*, *B*, and *C* of the Antoine Equation (eq 3) Obtained in This Work with Expression of the Temperature Range and Acentric Factors ω for Pure Compounds

compound	*A*	*B*	*C*	ω	$(\Delta T)/(\mathrm{K})$	ref
tert-butanol	6.60044	1238.69	85.99	0.614	330−370	ref 1
methyl methanoate	6.45012	1216.46	31.08	0.258	300−330	this work
	6.29529	1125.20	42.59			ref 9
methyl ethanoate	6.48259	1329.44	32.87	0.325	300−350	this work
	6.24410	1183.70	50.74			ref 9
	6.49340	1329.46	33.52		310−340	ref 17
methyl propanoate	6.24665	1257.33	55.10	0.332	320−370	this work
	6.06734	1170.24	64.40			ref 11
	6.60420	1478.55	30.07		335−360	ref 18
methyl butanoate	6.17134	1299.49	63.05	0.367	340−400	this work
	6.10644	1271.06	65.94			ref 11
	6.30360	1381.64	53.60		345−385	ref 19

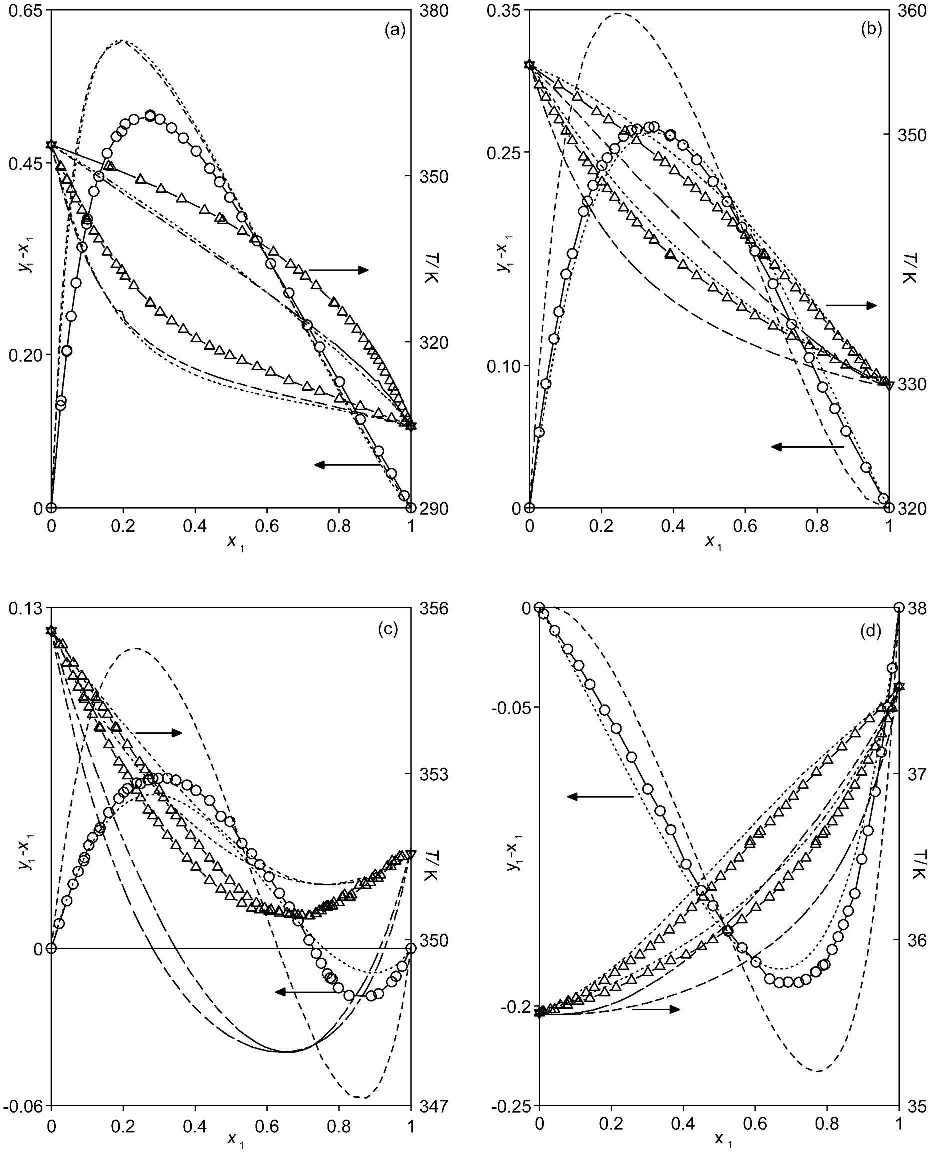

Figure 4. (a−d) Representation of VLE experimental values ($y_1 - x_1$) vs x_1 (○) and T vs x_1,y_1 (eq 6) for binary mixtures $C_{u-1}H_{2u-1}COOCH_3$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2) (a) for $u = 1$, (b) for $u = 2$, (c) for $u = 3$, and (d) for $u = 4$. Dashed lines represent the curves estimated with the UNIFAC model, (- - -) Hansen et al.[6] and (···) Gmehling et al.[7]

values are later used to characterize VLE data.

Presentation of VLE Data. The values obtained directly (p, T, x_1, y_1) in the isobaric VLE experiment at a pressure of $p = (101.32 \pm 0.02)$ kPa for the four binary mixtures of ($x_1$methyl alkanoates (methanoate to butanoate) + $(1 - x_1)$*tert*-butanol) are compiled in Table 7. From these values, considering the nonideal behavior of the vapor phase, the activity coefficients of the components of the liquid phase are estimated by

$$\ln \gamma_i = \ln\left(\frac{p y_i}{p_i^{\mathrm{o}} x_i}\right) + \frac{(B_{ii} - V_i^{\mathrm{o}})(p - p_i^{\mathrm{o}})}{RT} + \frac{p}{RT}\sum_j \sum_k y_j y_k (2\delta_{ji} - \delta_{jk}) \quad (5)$$

Table 7. Experimental Data $T-x_1-y_1$ and Calculated Quantities for the VLE of the Binary Mixtures of Methyl Alkanoate (1) + *tert*-Butanol (2) at 101.32 kPa

T/K	x_1	y_1	γ_1	γ_2	$\{G_m^E\}/\{RT\}$	T/K	x_1	y_1	γ_1	γ_2	$\{G_m^E\}/\{RT\}$
Methyl Methanoate (1) + *tert*-Butyl Alcohol (2)											
351.71	0.0257	0.1592	1.516	1.000	0.011	325.38	0.3020	0.8091	1.354	1.002	0.093
351.51	0.0273	0.1671	1.506	1.000	0.011	323.79	0.3344	0.8302	1.318	1.011	0.099
349.34	0.0431	0.2474	1.491	1.000	0.017	322.24	0.3670	0.8496	1.289	1.017	0.104
349.16	0.0434	0.2488	1.496	1.006	0.023	320.60	0.4029	0.8685	1.264	1.025	0.109
347.59	0.0553	0.3054	1.499	1.003	0.025	319.25	0.4402	0.8832	1.229	1.041	0.113
345.85	0.0688	0.3623	1.495	1.002	0.030	318.35	0.4675	0.8927	1.204	1.053	0.114
343.79	0.0855	0.4258	1.492	1.000	0.035	317.52	0.4959	0.9011	1.177	1.071	0.115
342.34	0.0981	0.4687	1.487	0.997	0.037	316.64	0.5299	0.9097	1.144	1.098	0.115
341.94	0.1002	0.4771	1.498	1.001	0.041	315.46	0.5720	0.9204	1.115	1.133	0.115
339.97	0.1182	0.5311	1.491	0.996	0.044	314.53	0.6100	0.9286	1.087	1.172	0.113
338.56	0.1321	0.5646	1.474	0.999	0.050	312.98	0.6607	0.9411	1.072	1.209	0.110
336.24	0.1550	0.6178	1.466	0.998	0.057	311.83	0.7112	0.9498	1.045	1.290	0.104
333.99	0.1810	0.6655	1.441	0.997	0.063	311.05	0.7460	0.9559	1.029	1.346	0.097
332.91	0.1961	0.6875	1.417	0.997	0.066	309.68	0.8009	0.9657	1.015	1.442	0.085
331.81	0.2056	0.7064	1.434	0.997	0.071	308.31	0.8587	0.9755	1.003	1.569	0.066
330.12	0.2295	0.7362	1.407	0.999	0.078	307.03	0.9098	0.9846	0.999	1.663	0.045
327.06	0.2749	0.7856	1.373	0.998	0.086	306.18	0.9456	0.9907	0.997	1.750	0.027
326.92	0.2751	0.7875	1.381	0.996	0.086	305.34	0.9810	0.9968	0.996	1.811	0.008
Methyl Ethanoate (1) + *tert*-Butyl Alcohol (2)											
353.94	0.0266	0.0797	1.432	1.005	0.015	340.37	0.3908	0.6522	1.187	1.050	0.097
352.96	0.0458	0.1329	1.426	1.003	0.019	340.28	0.3926	0.6549	1.190	1.049	0.097
351.81	0.0683	0.1871	1.390	1.007	0.029	339.49	0.4266	0.6815	1.168	1.060	0.100
351.17	0.0819	0.2197	1.386	1.006	0.032	338.63	0.4649	0.7095	1.146	1.076	0.102
350.25	0.1016	0.2658	1.388	1.002	0.035	337.66	0.5105	0.7398	1.122	1.099	0.105
349.48	0.1193	0.2979	1.354	1.008	0.043	336.86	0.5498	0.7649	1.104	1.118	0.105
348.16	0.1502	0.3585	1.345	1.006	0.049	336.11	0.5900	0.7872	1.085	1.149	0.105
347.73	0.1614	0.3768	1.332	1.007	0.052	335.44	0.6268	0.8073	1.070	1.177	0.103
347.09	0.1767	0.4033	1.327	1.008	0.057	334.58	0.6772	0.8346	1.052	1.214	0.097
346.17	0.2013	0.4418	1.311	1.009	0.062	333.77	0.7288	0.8578	1.032	1.288	0.091
345.63	0.2161	0.4621	1.298	1.013	0.066	333.03	0.7776	0.8831	1.020	1.336	0.079
344.92	0.2368	0.4891	1.280	1.017	0.071	332.50	0.8149	0.8997	1.008	1.411	0.071
344.07	0.2615	0.5226	1.270	1.017	0.075	331.90	0.8489	0.9186	1.008	1.442	0.062
343.38	0.2829	0.5482	1.258	1.020	0.079	331.47	0.8799	0.9338	1.003	1.505	0.051
342.87	0.2994	0.5655	1.245	1.026	0.083	330.73	0.9356	0.9641	0.998	1.575	0.027
341.90	0.3323	0.5997	1.225	1.033	0.089	330.10	0.9839	0.9904	0.995	1.735	0.004
341.50	0.3465	0.6143	1.218	1.034	0.090						
Methyl Propanoate (1) + *tert*-Butyl Alcohol (2)											
355.33	0.0220	0.0314	1.283	1.000	0.005	351.07	0.4401	0.4965	1.150	1.071	0.100
355.00	0.0433	0.0614	1.287	1.003	0.014	350.91	0.4715	0.5218	1.133	1.085	0.102
354.76	0.0609	0.0854	1.281	1.005	0.019	350.78	0.4965	0.5448	1.128	1.090	0.103
354.56	0.0748	0.1041	1.279	1.006	0.024	350.66	0.5299	0.5699	1.109	1.108	0.103
354.38	0.0901	0.1235	1.266	1.008	0.029	350.57	0.5566	0.5927	1.101	1.117	0.103
354.34	0.0924	0.1270	1.271	1.008	0.029	350.54	0.5792	0.6111	1.092	1.125	0.101
354.20	0.1043	0.1436	1.279	1.007	0.032	350.51	0.6053	0.6326	1.083	1.135	0.098
354.07	0.1146	0.1568	1.275	1.008	0.035	350.48	0.6341	0.6551	1.071	1.151	0.095
353.84	0.1332	0.1781	1.255	1.013	0.041	350.45	0.6617	0.6775	1.062	1.166	0.092
353.82	0.1359	0.1819	1.257	1.012	0.042	350.44	0.6864	0.6969	1.053	1.183	0.089
353.52	0.1597	0.2115	1.255	1.015	0.049	350.43	0.7162	0.7193	1.042	1.212	0.084
353.21	0.1879	0.2451	1.247	1.017	0.056	350.47	0.7365	0.7345	1.034	1.234	0.079
353.07	0.2014	0.2609	1.244	1.018	0.059	350.52	0.7506	0.7446	1.026	1.251	0.075
352.96	0.2120	0.2729	1.240	1.020	0.061	350.58	0.7676	0.7579	1.019	1.271	0.070
352.70	0.2371	0.3001	1.229	1.024	0.067	350.60	0.7755	0.7642	1.017	1.279	0.068
352.56	0.2484	0.3112	1.221	1.029	0.071	350.61	0.7809	0.7692	1.016	1.283	0.067
352.34	0.2690	0.3332	1.215	1.033	0.076	350.67	0.7983	0.7832	1.010	1.306	0.062
352.24	0.2821	0.3469	1.210	1.034	0.078	350.77	0.8278	0.8098	1.004	1.337	0.053
352.11	0.2975	0.3623	1.203	1.037	0.081	351.03	0.8892	0.8710	0.997	1.397	0.034
351.88	0.3228	0.3877	1.195	1.042	0.086	351.11	0.9099	0.8926	0.996	1.427	0.028
351.70	0.3465	0.4106	1.185	1.047	0.089	351.32	0.9464	0.9336	0.995	1.472	0.015
351.47	0.3773	0.4396	1.173	1.055	0.093	351.42	0.9583	0.9476	0.994	1.487	0.011
351.31	0.4024	0.4626	1.163	1.061	0.096	351.50	0.9753	0.9684	0.995	1.5103	0.006
Methyl Butanoate (1) + *tert*-Butyl Alcohol (2)											
355.66	0.0112	0.0080	1.324	1.000	0.003	363.81	0.6915	0.5035	1.026	1.197	0.073
355.80	0.0426	0.0310	1.342	1.004	0.016	364.40	0.7208	0.5326	1.021	1.220	0.071
356.04	0.0786	0.0577	1.342	1.005	0.028	364.91	0.7409	0.5542	1.017	1.232	0.067
356.28	0.1092	0.0801	1.329	1.006	0.037	365.72	0.7674	0.5845	1.010	1.244	0.058
356.46	0.1403	0.1017	1.305	1.011	0.047	365.91	0.7693	0.5864	1.004	1.240	0.053
356.79	0.1813	0.1298	1.274	1.016	0.057	366.34	0.7881	0.6085	1.004	1.259	0.052
357.11	0.2134	0.1527	1.259	1.018	0.063	366.51	0.7939	0.6147	1.001	1.267	0.050
357.53	0.2561	0.1810	1.226	1.024	0.070	367.09	0.8135	0.6418	1.002	1.276	0.047
358.01	0.3012	0.2101	1.190	1.033	0.075	367.62	0.8303	0.6650	1.000	1.288	0.043
358.37	0.3356	0.2335	1.173	1.041	0.080	368.07	0.8449	0.6857	1.000	1.303	0.041
358.72	0.3655	0.2539	1.157	1.048	0.083	368.62	0.8586	0.7063	0.996	1.311	0.035
359.08	0.4077	0.2789	1.125	1.071	0.089	369.29	0.8767	0.7331	0.992	1.336	0.029

Table 7. (Continued)

T/K	x_1	y_1	γ_1	γ_2	$\{G_m^E\}/\{RT\}$	T/K	x_1	y_1	γ_1	γ_2	$\{G_m^E\}/\{RT\}$
					Methyl Butanoate (1) + *tert*-Butyl Alcohol (2)						
359.58	0.4505	0.3085	1.108	1.087	0.092	370.07	0.8961	0.7698	0.995	1.332	0.026
360.00	0.4825	0.3328	1.100	1.097	0.094	370.80	0.9136	0.8016	0.994	1.348	0.021
360.58	0.5237	0.3614	1.080	1.117	0.093	371.61	0.9335	0.8411	0.996	1.366	0.017
361.19	0.5633	0.3925	1.069	1.134	0.092	372.40	0.9505	0.8779	0.998	1.374	0.013
361.92	0.6019	0.4239	1.055	1.150	0.088	373.29	0.9676	0.9175	0.997	1.378	0.008
362.56	0.6401	0.4537	1.039	1.179	0.084	373.94	0.9809	0.9505	1.000	1.374	0.006
363.16	0.6664	0.4781	1.032	1.190	0.079						

where $\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$ and where the second virial coefficients B_{ij} for pure compounds and mixtures are estimated by the correlations proposed by Tsonopoulos.[21] The molar volumes V_i^o of each pure component i at each equilibrium temperature are calculated using Rackett's equation with the modification proposed by Spencer and Danner[22] using the Z_{RA} coefficient values compiled in Reid et al.[23] The activity coefficients obtained with eq 5 permit values to be obtained for the adimensional function of Gibbs $G_m^E = \sum x_i \ln \gamma_i$, and the results are presented in Table 7 for each binary system. A point-to-point version of the test proposed by Fredenslund et al.[24] was applied to all of the mixtures by evaluating the differences between the molar fractions of the vapor phase between the experimental value and that estimated by the method for each equilibrium point. The four systems in this work verify the overall condition imposed by the number of points N of each system $\bar{\delta} = \sum_i(y_{i,\mathrm{exp}} - y_{i,\mathrm{cal}})/N \leq 0.01$.

Figure 4 shows the quantities of T versus x_1,y_1 and ($y_1 - x_1$) versus x_1 for the four methyl alkanoate (1) + *tert*-butyl alcohol (2) systems. As mentioned in the Introduction, VLE data for the systems studied here have not been found in the literature. In Figure 4c, the methyl propanoate (1) + *tert*-butyl alcohol (2) mixture presents an azeotrope, which was determined with the conditions $(y_1 - x_1) = 0$ and $(\mathrm{d}T/\mathrm{d}x_1)_p = 0$. The position of this point was $x_{az} = 0.726$ and $T_{az} = 350.43$ K. Figure 3 shows the azeotrope for this mixture, and the inset shows the position of this point relative to others recorded in the literature[1,25] for other mixtures of methyl alkanoates with *tert*-butyl alcohol. The representation was done in reduced coordinates, considering a mixing rule to calculate the pseudocritical quantities of the geometric mean of the critical properties of the pure substances. The location of the azeotrope for the different mixtures of esters with *tert*-butyl alcohol and other *iso*-alkanols, in the representation of log $p_{i,r}^o$ versus $1/T_r$ or $1/x_{az}$, will be better clarified in future work.

Table 8. Parameters Obtained by Correlation of VLE and Excess Enthalpies Data Using Equation 11 between Parenthesis Is the Correlation Coefficient r^2

	mixtures[a]			
parameters	1	2	3	4
A_{01}	0.0001	0.009	−0.003	0.005
A_{02}	−0.073	1363.727	230.581	1423.128
A_{03}	0.001	−6.898	0.666	−5.251
A_{04}	454.554			
A$_{05}$	9.998			
A_{21}	0.0004	0.017	0.009	0.015
A_{22}	−0.195	3107.816	1988.417	1060.813
A_{23}	−0.478	−14.196	−8.247	−8.453
A_{24}	9396.734			
A_{25}	−11.910			
k	0.543	0.518	0.544	1.344
$s(G_m^E/RT)$	0.004(0.99)	0.004(0.99)	0.005(0.97)	0.003(0.98)
$s(\gamma_i)$	0.025(0.98)	0.024(0.98)	0.013(0.99)	0.016(0.98)
$s(H_m^E/RT)_{299.15}$	25.0(0.99)	83.1(0.98)	39.9(0.99)	82.2(0.97)
$s(H_m^E/RT)_{318.15}$		85.8(0.98)	39.8(0.99)	80.9(0.98)

[a] Columns: 1, methyl methanoate (1) + *tert*-butyl alcohol (2); 2, methyl ethanoate (1) + *tert*-butyl alcohol (2); 3, methyl propanoate (1) + *tert*-butyl alcohol (2); 4, methyl butanoate (1) + *tert*-butyl alcohol (2).

Treatment of VLE Data. Isobaric VLE data and excess enthalpies at two temperatures were correlated simultaneously with an equation that had been presented in previous work[1,5] similar to eq 1, which when applied to Gibbs' adimensional function for a binary mixture has the form

$$\frac{G_m^E}{RT}(T, x_1) = z_1 z_2 \sum_{i=0}^{m} b_i z_1^i \tag{6}$$

where the b_i coefficients are temperature-dependent. This dependence can be expressed in different ways, but in previous work,[5] a relationship was established depending on the polynomial form imposed at $C_p^E = \phi(T)$. It was shown that a standard relationship of the coefficients of eq 6 with temperature, which gives good results in the correlation of VLE data, has the form

$$b_i = A_{i1}T + \frac{A_{i2}}{T} + A_{i3} \tag{7}$$

which is the results of considering that the variation between the excess thermal capacity and temperature is a straight line. Nevertheless, this relationship can be adapted to each case depending on the difficulty of the correlation concerned. The thermodynamic equation that relates the two quantities H_m^E and G_m^E is formulated by

$$-\frac{H_m^E}{RT} = T\left[\frac{\partial(G_m^E/RT)}{\partial T}\right]_{p,x} \tag{8}$$

which can be applied to eq 6 to produce extended expressions for the Gibbs function and the excess enthalpy, considering now coefficients of the form in eq 7. The resulting equations are

$$\frac{G_m^E}{RT}(T, x_1) = z_1 z_2 \sum_{i=0}^{m}\left(A_{i1}T + \frac{A_{i2}}{T} + A_{i3}\right) z_1^i \tag{9}$$

$$\frac{H_m^E}{R}(T, x_1) = z_1 z_2 \sum_{i=0}^{m}(A_{i2} - A_{i1}T^2) z_1^i \tag{10}$$

However, from the experience obtained in this and in other work by applying eqs 9 and 10, it can be observed that an unnecessary overparametrization appears in the development of these polynomials in z_1. This fact can be avoid by considering only the even-powered terms for z_1; that is, terms in the above equations for which $i = 0, 2, 4$, ... Therefore, the simultaneous fit of the experimental data of the pairs (x_1, H_m^E) and (x_1, G_m^E) is done using a least-

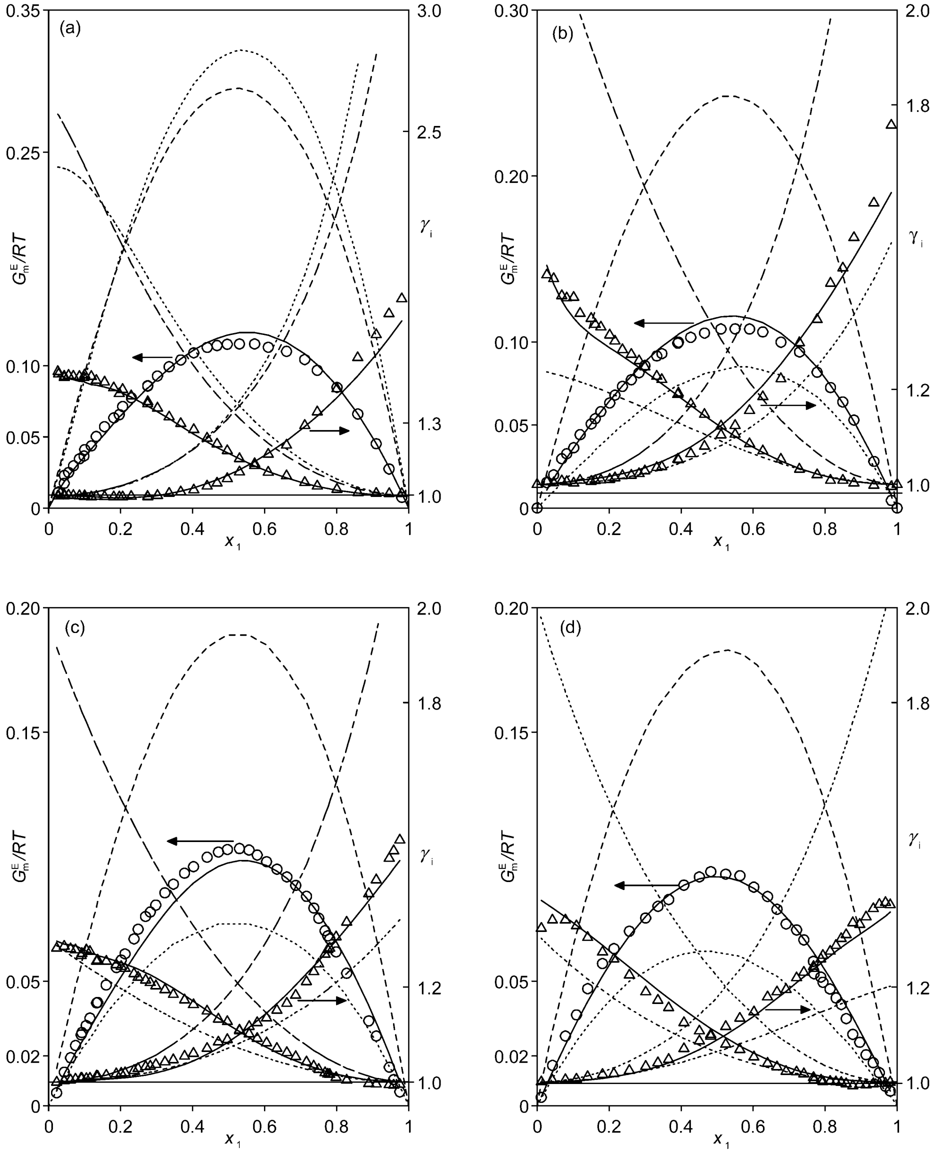

Figure 5. (a−d) Representation of experimental and fitting curves (−) for the quantities G_m^E/RT vs x_1 (○) and γ_i vs x_1 (△) for the binary mixtures $C_{u-1}H_{2u-1}COOCH_3$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2) (a) for $u = 1$, (b) for $u = 2$, (c) for $u = 3$, and (d) for $u = 4$. Dashed lines represent the values estimated by the UNIFAC model, (- - -) Hansen et al.[6] and (···) Gmehling et al.[7]

squares procedure. The objective function OF that must be minimized takes the form

$$\mathrm{OF} = \sum_{i=1}^{q}\left[\frac{H_m^E}{R}(T_i, x_{1i}) - \left(\frac{H_m^E}{R}\right)_i\right]^2 + \sum_{j=1}^{n}[\ln \gamma_1(T_j, x_{1j}) - \ln \gamma_{1j}]^2 + \sum_{j=1}^{n}[\ln \gamma_2(T_j, x_{1j}) - \ln \gamma_{2j}]^2 \quad (11)$$

and represents the sum of the squares of the differences between the corresponding quantities calculated by the model and those obtained from the experimental values. The OF defined by eq 11 does not take into account the values of the Gibbs function because these, calculated from the natural logarithms of the activity coefficients γ_i would not produce statistically independent information. Owing to the complexity of the expressions used here and to avoid the problem of multiplicity of roots, optimization of the OF that was established was done using a genetic algorithm,[26] which has been previously applied in a similar case.[1,5]

Table 8 shows the coefficients obtained for the model proposed in the correlation of experimental data of methyl alkanoate + *tert*-butanol mixtures. It can be observed that data fitting of the methyl methanoate + *tert*-butyl alcohol system improved with a wider model in which the b_i coefficients of the indices of z_1 are now

$$b_i = A_{i1}T^2 + A_{i2}T + A_{i3}\ln T + \frac{A_{i4}}{T} + A_{i5} \quad (12)$$

and that, according to previous observations, the form of this coefficient is the result of considering the thermal capacity to be a squared function of temperature. This Table also shows the statistical evaluation of the correlations, by the parameters that define the goodness of fit, s and r^2, for each case. In Figure 5a−d, the solid lines of the curves calculated with the model are shown next to the experimental equilibria data, revealing acceptable correlations and the worth of the procedure applied. Similarly, Figure 6a−d shows the discrepancies in H_m^E obtained with the curves resulting from the correlation procedure described and the experimental data, observing a good

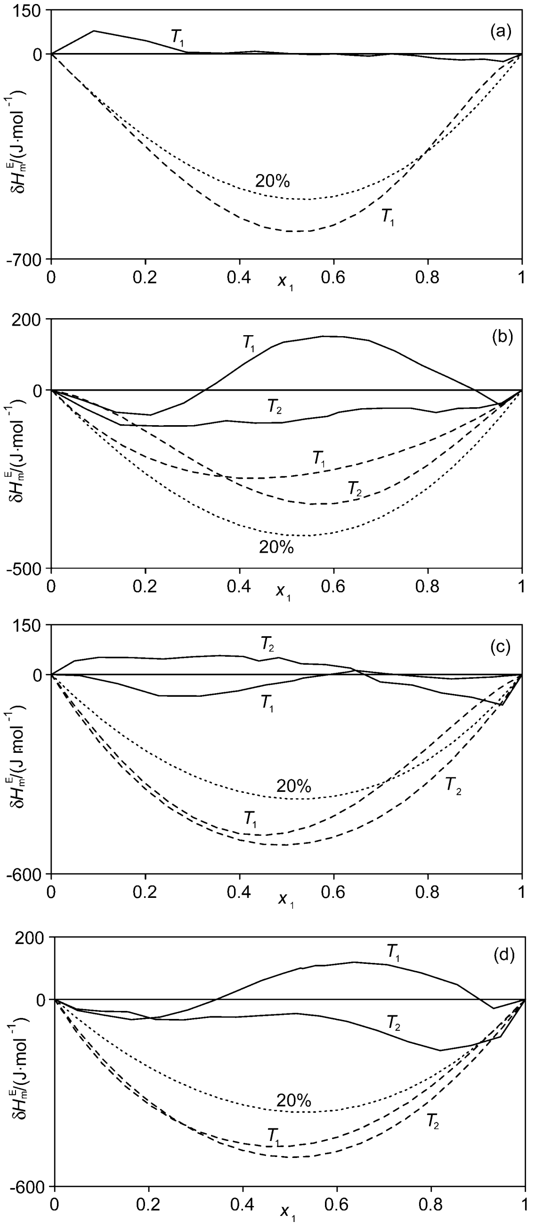

Figure 6. (a–d) Representation of the deviations $\delta H^E_m = H^E_{i,\text{calcd}} - H^E_{i,\text{exptl}}$ obtained as the differences between the calculated curve by the correlation of VLE values (solid lines) and those obtained by the UNIFAC model[7] (dashed lines) at the temperatures of $T_1 = 299.15$ K and $T_2 = 318.15$ K and the corresponding experimental values for the binary mixtures $C_{u-1}H_{2u-1}COOCH_3$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2) (a) for $u = 1$, (b) for $u = 2$, (c) for $u = 3$, and (d) for $u = 4$.

estimation for all cases, with differences close to the abscissa, especially for the one corresponding to the methyl methanoate + *tert*-butanol mixture in which the enthalpies are determined only at 299.15 K.

Prediction of VLE Data. In previous work,[1] the version proposed by Gmehling et al.[7] consisting of the UNIFAC method was used to study the validity of the method used to estimate isobaric VLE properties and enthalpies of the ethyl alkanoate + *tert*-butyl alcohol mixtures, concluding that this version was not effective at estimating characteristic VLE values and enthalpies, although the modified UNIFAC model[7] offers specific area and volume parameters for the OH− of a tertiary alcohol. In this work, with methyl alkanoate mixtures and the same alkanol, the UNIFAC model was used in two of the best known versions: the original one with the parameters proposed by Hansen et al.[6] and that of Gmehling et al.[7] The values estimated are recorded graphically in Figure 5a–d for the Gibbs function and the activity coefficients of VLE, and Figure 4a–d shows predictions of the models for equilibria concentrations and temperatures. Both models present an almost identical prediction for the mixtures formed by methyl methanoate, possibly for having used the same few systems described in the literature with this ester, to estimate parameters of the specific OH/COOH interaction. In both cases, estimations of the quantities of VLE (Figures 4a and 5a) are quite different from experimental values. For the other three mixtures, the version of Hansen et al.[6] produces estimations of G^E_m/RT and γ_i well above real values, above 100% in almost all cases. As can be seen in Figures 4b–d and 5b–d, this model even estimates azeotropes at extreme concentrations not obtained experimentally in the mixtures of methyl ethanoate and butanoate + *tert*-butyl alcohol, whereas this is predicted by a single point (x_{az}, T_{az}) in the mixture of methyl propanoate + *tert*-butyl alcohol of (0.632, 347.97) far from the experimental value (0.726, 350.43). The version of Gmehling et al.[7] gives values of G^E_m/RT and γ_i that are lower than experimental values for the mixtures of methyl ethanoate, propanoate, and butanoate + *tert*-butyl alcohol. The estimations of concentrations and temperatures can be considered to be acceptable. The azeotrope for the methyl propanoate mixture is estimated to be (0.760, 350.99) (Figure 4c). This method gives estimates of the enthalpies for the four mixtures that are lower than experimental values, with a mean error for all set above 20% with the exception of the methyl ethanoate + *tert*-butyl alcohol mixture, and producing a negative variation of this excess quantity with temperature, $(\partial H^E_m / \partial T)_{p,x} < 0$. Figure 6a–d shows the differences described above.

Conclusions

In this work, isobaric VLE at 101.32 kPa and excess quantities H^E_m and V^E_m are presented at two temperatures for four binary systems of methyl alkanoates (methanoate to butanoate) with *tert*-butyl alcohol. VLE values were consistent with the point-to-point method proposed by Fredenslund et al.[24] For the set of four mixtures, a single azeotrope was experimentally found in the mixture of methyl propanoate + *tert*-butyl alcohol with the following coordinates, $x_{az} = 0.726$ and $T = 350.43$ K. For the data correlation, an expression was used for the Gibbs adimensional function and a procedure that can improve the combined treatment of the VLE and excess enthalpy data. The full form of this equation is given by

$$\frac{G^E_m}{RT}(T, x_1) = z_1 z_2 \sum_i \left(A_{i1}T^2 + A_{i2}T + A_{i3}\ln T + \frac{A_{i4}}{T} + A_{i5} \right) z_1^i \qquad (i = 0, 2) \quad (13)$$

for the mixture of methyl methanoate + *tert*-butyl alcohol, but this is simpler, with only three A_{ij} coefficients in the other systems. Coefficients of the model (eq 13) were estimated using the γ_i and H^E_m, minimizing an objective function established with a least-squares method (eq 11) and implementing a genetic algorithm. Its application in this work gave excellent results; therefore, the procedure developed seems to be suitable for the treatment of VLE data in future work.

Predictions of the VLE and enthalpies with two versions of the UNIFAC model, Hansen et al.[6] and Gmehling et al.,[7] are recorded qualitatively in Figures 4−6. Both versions of the model give similar values that are different from experimental values in the case of the methyl methanoate mixture. However, for the other mixtures very different results are obtained for both versions. Hence, the version of Hansen et al.[6] produces values of G_m^E/RT and γ_i that are higher than experimental values whereas the version of Gmehling et al.[7] with the modified UNIFAC predicts the G_m^E/RT and the γ_i as being lower than experimental values, but in this case, they are more acceptable than values from the other version. The H_m^E values predicted by this method are also much lower. Determining new VLE data for ester + alkanol mixtures of this nature can help to improve estimations made by these predictive methods.

Literature Cited

(1) Ortega, J.; Espiau, F.; Postigo, M. Isobaric Vapor−Liquid Equlibria and Excess Quantities for Binary Mixtures of an Ethyl Ester + *tert*-Butyl Alcohol and a New Approach to VLE Data Processing. *J. Chem. Eng. Data* **2003**, *48*, 916−924.

(2) Ortega, J.; Hernández, P. Thermodynamic Study of Binary Mixtures Containing an Isobutylalkanol and an Alkyl (Ethyl to Butyl) Alkanoate (Methanoate to Butanoate), Contributing with Experimental Values of Excess Molar Enthalpies and Volumes, and Isobaric Vapor−Liquid Equilibria. *J. Chem. Eng. Data* **1999**, *44*, 757−771.

(3) González, E.; Ortega, J. Vapor-liquid equilibria at 101.32 kPa in mixtures formed by the first four butyl alkanoates and butan-2-ol. *Fluid Phase Equilib.* **1996**, *124*, 161−175.

(4) Hernández, P.; Ortega, J. Vapor−Liquid Equilibria and Densities for Ethyl Esters (Ethanoate to Butanoate) and Alkan-2-ol (C_3−C_4) at 101.32 kPa. *J. Chem. Eng. Data* **1997**, *42*, 1090−1100.

(5) Ortega, J.; Espiau, F. A New Correlation Method for Vapor-Liquid Equilibria and Excess Enthalpies for Nonideal Solutions Using a Genetic Algorithm. Application to Ethanol+an *n*-Alkane Mixtures. *Ind. Eng. Chem. Res.* **2003**, *42*, 4978−4992.

(6) Hansen, H. K.; Rasmussen, P.; Fredenslund, Aa.; Schiller, M.; Gmehling, J. Vapor-Liquid Equilibria by UNIFAC Group-Contribution. 5. Revision and Extension. *Ind. Eng. Chem. Res.* **1991**, *30*, 2355−2358.

(7) Gmehling, J.; Li, J.; Schiller, M. A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Chem. Eng. Res.* **1993**, *32*, 178−193.

(8) Wilhoit, R. C.; Zwolinski, B. J. Physical and Thermodynamic Properties of Aliphatic Alcohols. *J. Phys. Chem. Ref. Data.* **1973**, *2*, 117.

(9) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; Techniques of Chemistry; Wiley-Interscience: New York, 1986; Vol. II.

(10) Dauber, T. E.; Danner, R. P. *Data Compilation Tables of Properties of Pure Compounds*; AIChE/DIPPR: New York, 1984.

(11) *TRC Thermodynamic Tables Non-Hydrocarbons*; Thermodynamic Research Center: Texas A&M University System: College Station, TX, 1965.

(12) Ortega, J.; Espiau, F.; Tojo, J.; Canosa, J.; Rodríguez, A. Isobaric Vapor−Liquid Equilibria and Excess Properties for the Binary Systems of Methyl Esters + Heptane. *J. Chem. Eng. Data*. **2003**, *48*, 1183−1190.

(13) Ortega, J.; Espiau, F.; Toledo, F. Thermodynamic properties of (an ester + an alkane). XVI. Experimental H^E and V^E values and a new correlation method for (an alkyl ethanoate + an alkane) at 318.15 K. *J. Chem. Thermodyn*. **2004**, *36*, 193−209.

(14) Ortega. J.; Alcalde, R. Determination and algebraic representation of volumes of mixing at 298.15 K of methyl alkanoates (from ethanoate to pentadecanoate) with pentadecane. *Fluid Phase Equilib*. **1992**, *71*, 49−71.

(15) Ortega, J.; Toledo, F. J. Thermodynamic properties of (an ethyl ester + a branched alkane). XV. H^E and V^E values for (an ester + an alkane). *J. Chem. Thermodyn*. **2002**, *34*, 1439−1459.

(16) Bondi, A. *Physical Properties of Molecular Liquids, Crystals and Glasses*; Wiley: New York, 1968.

(17) Ortega, J.; Susial, P. VLE at 114.66 and 127.99 kPa for the systems methyl acetate + ethanol and methyl acetate + propan-1-ol. Measurements and prediction. *J. Chem. Eng. Jpn*. **1990**, *23*, 621−626.

(18) Ortega, J.; Susial, P. Measurements and prediction of VLE of methyl propanoate/ethanol/propan-1-ol at 114.66 and 127.99 kPa. *J. Chem. Eng. Jpn*. **1990**, *23*, 349−353.

(19) Ortega, J.; Susial, P.; de Alfonso, C. Isobaric Vapor−Liquid Equilibrium of Methyl Butanoate with Ethanol and 1-Propanol Binary Systems. *J. Chem. Eng. Data* **1990**, *35*, 216−219.

(20) Ortega, J.; González, C.; Peña, J.; Galván, S. Thermodynamic study on binary mixtures of propyl ethanoate and alkan-1-ol (C_2−C_4). Isobaric vapor-liquid equilibria and excess properties. *Fluid Phase Equilib*. **2000**, *170*, 87−111.

(21) Tsonopoulos, C. An Empirical Correlation of Second Virial Coefficients. *AIChE J*. **1974**, *20*, 263−272.

(22) Spencer, C. F.; Danner, R. P. Improved Equation for Prediction of Saturated Liquid Density. *J. Chem. Eng. Data*. **1972**, *17*, 236−241.

(23) Reid, R. C.; Prausnitz, J.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1988

(24) Frendenslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC: A Group Contribution Method*; Elsevier: Amsterdam, 1977.

(25) Gmehling, J.; Bölts, R. Azeotropic Data for Binary and Ternary Systems at Moderate Pressures. *J. Chem. Eng. Data* **1996**, *41*, 202−209.

(26) Gen, M.; Cheng, R. *Genetic Algorithms and Engineering Design*; John Wiley & Sons: New York, 1997.

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