Correlation and Prediction of Excess Quantities and Vapor−Liquid Equilibria of Alkyl Esters + *tert*-Butyl Alcohol: Experimental Data for Propyl Esters + *tert*-Butyl Alcohol

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In this work, the experimental values for excess quantities H_m^E and V_m^E are presented at two temperatures and the isobaric vapor−liquid equilibrium data (VLE) at 101.32 kPa for binary systems comprised of the first four propyl alkanoates with *tert*-butyl alcohol. It was demonstrated for the four mixtures that $(\partial H_m^E/\partial T)_{p,x} < 0$ and $(\partial V_m^E/\partial T)_{p,x} > 0$. Experimental data of VLE were checked with the Fredenslund method, which showed the systems to be thermodnamically consistent. Only the binary mixture (propyl methanoate + *tert*-butyl alcohol) presented an azeotropic point at ester concentration of 0.621 and at a temperature of 350.52 K. Simultaneous correlations are performed with the VLE data and the excess enthalpies with different known thermodynamic mathematical models (Wilson, NRTL, and UNIQUAC) with temperature-dependent coefficients and another polynomial model proposed by our research group. The latter gave the most acceptable correlation for the mixtures studied. The original UNIFAC model, with the interaction parameters of Hansen et al. (*Ind. Eng. Chem. Res*. **1991**, *30*, 2355−2358), did not give good VLE predictions, while the version of Gmehling et al. (*Ind. Eng. Chem. Res*. **1993**, *32*, 178−193) produced acceptable estimations of VLE data, except for methanoates. Estimations of excess enthalpies with this model always produced lower values with an average error of 20 %. In this work, the results obtained for the 16 mixtures (alkyl esters + *tert*-butyl alcohol) are evaluated.

Introduction

In the three previous works,[1−3] data of thermodynamic quantities of binary liquid systems, comprised of different alkyl alkanoates with *tert*-butyl alcohol, were presented. These works form part of an extensive research project of several years duration for which our research team has published a wealth of information about binary systems of esters and primary (methanol to butanol) or secondary alkanols (propanol, butanol) and, finally, with the tertiary alkanol of butanol; all conducted in a highly systematic manner. With this paper, we carry out a global analysis of the results from previous works[1−3] in order to evaluate the behavior of these mixtures. To do this, we present here the enthalpy data H_m^E measured at 299.15 and 318.15 K, the volumes V_m^E measured at 303.15 and 318.15 K, and the vapor−liquid equilibria (VLE) measured at a constant pressure of 101.32 kPa for a set of four binary mixtures comprised of propyl esters (methanoate to butanoate) with the tertiary butyl alcohol. There are not data published in the literature of the mentioned properties.

Another objective of this series of works has been to introduce a method for the experimental treatment of data. This was presented in the first of this set of papers,[1] and its efficacy will be confirmed again here. To verify the goodness of the proposed treatment, the data produced will be compared with those obtained by classical methods (Wilson, NRTL, and UNIQUAC), which use temperature-dependent parameters and are the methods most commonly used to treat VLE data.

Another objective initially proposed with this series of works with *tert*-butyl alcohol was to verify the predictive capacity of the UNIFAC engineering group contribution method, since we considered it to be of interest to study its application on mixtures containing a tertiary alkanol. The oldest version of the model, with parameters of Hansen et al.,[4] to predict isobaric VLE data is simpler and more restricted and has, so far, produced unacceptable results in the mixtures studied previously. In the papers published in this series,[1−3] the need to recalculate parameters of ester/alkanol interaction was mentioned. We will consider doing this soon when we have sufficient VLE data, not only of esters + alkanols but also of the primary systems ester/alkane mixtures since it is essential to define the primary CH_2/COO interaction. Another version of the UNIFAC model, the one proposed by Gmehling et al.,[5] offers better predictions for this type of model, both for VLE properties and for excess enthalpies. This improvement could possibly be due to fact that this latter version presents exclusive values for the group volume R_k and area Q_k parameters for a tertiary alkanol. However, despite this, our research into ester/alkanol mixtures has revealed that the model has a different versatility depending on whether the ester corresponds to a methanoate, to an ethanoate, or to other alkyl alkanoates.

Experimental Section

Materials. The pure substances used in this research, the propyl esters and *tert*-butyl alcohol, were supplied by Aldrich and were of the highest commercial purity. Nonetheless, before using them in the experiments, all products were subjected to a preliminary treatment that consisted of desgassifying with ultrasound, followed by desiccation for several days with a molecular sieve, type 3A from Fluka, to eliminate any trace of

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Table 1. Physical Properties of Pure Compounds

compound	mass fraction	$T^{o}_{b,exp}$ / K	$T^{o}_{b,lit}$ / K	T / K	ρ_{exp} / $kg \cdot m^{-3}$	ρ_{lit} / $kg \cdot m^{-3}$	$n_{D,exp}$	$n_{D,lit}$
tert-butyl alcohol	0.997	355.55	355.50[a]	303.15→	775.37	775.45[a] 775.7[b]	1.3822	1.3823[b]
			355.57[b]	318.15→	759.87	759.45[a]	1.3741	
propyl methanoate	0.99	353.90	353.97[a,c]	303.15→	893.84	894.06[a] 893.8[d]	1.3718	
				318.15→	875.56	875.9[e]	1.3650	
propyl ethanoate	0.99	374.55	374.69[a] 374.65[c]	303.15→	876.29	877.16[a] 876.9[d]	1.3792	
				318.15→	859.78	859.6[e]	1.3723	
propyl propanoate	0.98	395.55	395.65[c,d]	303.15→	870.30	871.7[d]	1.3882	
				318.15→	854.52	856.4[e]	1.3812	
propyl butanoate	0.99	416.41	416.45[c,d]	303.15→	862.94	863.3[d]	1.3950	
				318.15→	848.25	848.5[e]	1.3885	

[a] Ref 6. [b] Ref 8. [c] Ref 7. [d] TRC.[9] [e] Values obtained by interpolation from TRC.[9]

moisture. After this, the quality of the substances was verified with a GC model HP-6890 equipped with FID, and the resulting purity values for all the substances coincided with those indicated by the manufacturer. Table 1 shows the average values for the physical properties of all the compounds, so the normal boiling point ($T^{o}_{b,i}$) was determined at a pressure of 101.32 kPa with the same equilibrium ebullometer, giving values very similar to those recorded in the literature. When studying solutions, it is usual practice to present the characteristics of the pure compounds measured at a standard temperature of 298.15 K. However, since *tert*-butyl alcohol has a melting point recorded in the literature[6] of 298.81 K, in this case, to characterize the quality of the products used, measurements of densities (ρ) and refractive indices (n_D) were obtained at temperatures of 303.15 K and 318.15 K. In the literature,[6−9] with only some exception, direct experimental data of physical properties at those temperatures have not been found for the propyl esters used in this work. It is, therefore, not possible to explain the differences appreciated in the interpolated data.

Apparatus and Procedures. Excess enthalpies (H^{E}_{m}) of the binary mixtures (propyl esters + *tert*-butyl alcohol) were determined isothermically at temperatures of 299.15 K and 318.15 K. The uncertainty in the calorimeter temperature used, type Calvet model MS80D by Setaram, was ± 0.01 K, and the equipment was electrically calibrated regularly at the two working temperatures with a Joule effect. The uncertainty in the experimental results was estimated to be lower than 1 % for the H^{E}_{m} and of $\pm 2 \cdot 10^{-4}$ for the molar fractions x of the corresponding propyl ester. The functioning of the experimental system was verified only at 318.15 K by comparing the experimental H^{E}_{m} values obtained in all concentrations range for the ethanol + nonane mixture. Our values giving place to H^{E}_{m} values whose differences with those from literature[10] were lower than 1 %, the uncertainty indicated above for the apparatus.

To obtain experimental values, $p-T-x-y$, of the isobaric VLE for the four binary mixtures, a small glass ebullometer was used, around 60 cm^3, which operated in continuum way recirculating both phases. The following procedure is used to obtain each of the variables: control and measurement of pressure, kept constant at (101.32 ± 0.02) kPa, this was done by using a controller/calibrator, model PPC2, supplied by Desgranges et Huot, that presents an uncertainty better than ± 0.02 kPa. The other intensive variable, the temperature of each equilibrium stage, was measured with an ASL-F25 thermometer, calibrated regularly according to the ITS-90, which presented an uncertainty of around ± 10 mK. When the equilibrium was reached between the two phases, observing the constancy of pressure (p) and temperature (T), which is achieved after a mean time interval of 30 to 40 min, samples were extracted from the liquid phase and the condensed vapor phase. The respective concentrations of these in ester, x_1 and y_1, respectively, are determined indirectly via the densities of the binaries propyl esters (1) + *tert*-butyl alcohol (2). Previously, correlations $\rho = \rho(x_1)$ were obtained for each of the mixtures at the two temperatures of 303.15 and 318.15 K, using synthetic samples, of known composition, and the type of correlation used corresponded to a simple equation of the following type:

$$\rho = \sum_{i=1}^{2} x_i \rho_i + x_i x_j \sum_{i=0}^{2} a_i {x_1}^{i}$$

A digital densimeter Anton Paar, model DMA60/602, calibrated with water and nonane and with a uncertainty of ± 0.02 kg·m^{-3}, was used to measure densities of both pure substances and mixtures. The pairs (x_1, ρ) were also used to calculate the excess volumes. The experimentation was, therefore, validated by analyzing the adequate representation of the data (x_1, V^{E}_{m}), and the uncertainty in the calculations of these pairs of values was of ($\pm 5 \cdot 10^{-5}$, $\pm 2 \cdot 10^{-9}$ m^3·mol^{-1}). Calculation of concentrations x_1 and y_1 for each of the phases using the previous equation, with known densities of the samples extracted from liquid and vapor phases, respectively, had an uncertainty better than ± 0.002 units in the ester mole fraction.

Results

Excess Properties. Table 2 shows the data (x_1, V^{E}_{m}) corresponding to the direct measurements of the concentration and density for each of the binary mixtures of propyl esters (1) + *tert*-butyl alcohol (2), determined at temperatures of 303.15 and 318.15 K, while Table 3 records the values obtained in the direct experimentation of enthalpies (x_1, H^{E}_{m}) for the same mixtures, measured at temperatures of 299.15 and 318.15 K. For the density and enthalpy measurements, the election of the first working temperatures was justified in the previous section to avoid the solidification of *tert*-butyl alcohol at $T^{o}_{m,i} = 298.81$ K. Figures 1 and 2 show the experimental values of V^{E}_{m} and H^{E}_{m} versus the ester concentration. The variation in these with alkyl ester chain and with temperature, at equimolar concentration, appears in the corresponding insets.

In the series of VLE papers conducted to date with *tert*-butyl alcohol,[1−3] a fourth-order equation was used to correlate the thermodynamic data of the excess quantities of each system.

Table 2. Excess Molar Volumes, V^{E}_{m}, for Binary Systems of Propyl Esters (1) + *tert*-Butyl Alcohol (2) at Two Different Temperatures

x_1	$\frac{10^9 \cdot V^E_m}{m^3 \cdot mol^{-1}}$	x_1	$\frac{10^9 \cdot V^E_m}{m^3 \cdot mol^{-1}}$	x_1	$\frac{10^9 \cdot V^E_m}{m^3 \cdot mol^{-1}}$
303.15 K					
Propyl Methanoate (1) + *tert*-Butyl Alcohol (2)					
0.0613	232	0.4040	749	0.7634	533
0.1022	352	0.4646	760	0.8152	454
0.1561	481	0.5126	751	0.8518	382
0.2147	586	0.5729	718	0.9058	267
0.2631	658	0.6100	698	0.9558	142
0.3110	704	0.6562	668		
0.3604	732	0.7206	582		
Propyl Ethanoate (1) + *tert*-Butyl Alcohol (2)					
0.0592	174	0.4083	715	0.7481	525
0.0987	277	0.4512	726	0.8180	412
0.1549	402	0.5076	723	0.8690	312
0.1964	484	0.5677	702	0.9167	207
0.2539	575	0.6144	672	0.9469	135
0.3093	643	0.6505	641		
0.3593	687	0.7060	583		
Propyl Propanoate (1) + *tert*-Butyl Alcohol (2)					
0.0519	128	0.4065	563	0.6623	521
0.0971	219	0.4170	561	0.7079	478
0.1468	313	0.4435	569	0.7473	436
0.1972	385	0.5157	570	0.8144	348
0.2460	449	0.5510	565	0.8578	281
0.3032	502	0.5642	560	0.9001	207
0.3540	532	0.6113	549	0.9394	136
Propyl Butanoate (1) + *tert*-Butyl Alcohol (2)					
0.0472	101	0.4039	555	0.6402	529
0.1057	218	0.4461	563	0.6915	494
0.1522	302	0.4593	573	0.7449	440
0.1960	360	0.4895	571	0.7992	374
0.2531	437	0.5459	565	0.8526	284
0.2929	479	0.5540	568	0.9028	198
0.3508	528	0.5931	555	0.9597	87
318.15 K					
Propyl Methanoate (1) + *tert*-Butyl Alcohol (2)					
0.0501	208	0.3889	765	0.7401	597
0.1178	408	0.4438	781	0.7996	499
0.1718	530	0.5033	774	0.8551	404
0.2218	609	0.5574	763	0.9117	270
0.2859	691	0.6203	729		
0.3445	734	0.6780	663		
Propyl Ethanoate (1) + *tert*-Butyl Alcohol (2)					
0.0724	217	0.3580	679	0.7098	597
0.1084	316	0.4059	712	0.7775	513
0.1406	382	0.4689	727	0.8290	419
0.1989	495	0.5226	723	0.9060	257
0.2600	576	0.5801	699		
0.3076	627	0.6377	657		
Propyl Propanoate (1) + *tert*-Butyl Alcohol (2)					
0.0468	86	0.3149	466	0.6761	531
0.0882	177	0.3684	518	0.7366	477
0.1301	234	0.4016	551	0.8205	387
0.1715	302	0.4898	584	0.9010	230
0.2283	383	0.5525	577		
0.2828	443	0.6085	565		
Propyl Butanoate (1) + *tert*-Butyl Alcohol (2)					
0.0350	86	0.2956	468	0.6439	539
0.0730	166	0.3301	501	0.7150	482
0.1085	243	0.4003	542	0.8068	388
0.1678	352	0.4560	561	0.8966	239
0.2108	385	0.5182	565	0.9299	169
0.2620	434	0.5871	561		

Table 3. Excess Molar Enthalpies, H^{E}_{m}, for Binary Systems of Propyl Esters (1) + *tert*-Butyl Alcohol (2) at Two Different Temperatures

x_1	$\frac{H^E_m}{J \cdot mol^{-1}}$	x_1	$\frac{H^E_m}{J \cdot mol^{-1}}$	x_1	$\frac{H^E_m}{J \cdot mol^{-1}}$
299.15 K					
Propyl Methanoate (1) + *tert*-Butyl Alcohol (2)					
0.0586	472.1	0.4261	1982.4	0.6910	1725.0
0.1196	915.6	0.4696	2015.3	0.7439	1544.2
0.1857	1281.5	0.5063	2015.9	0.7982	1297.1
0.2507	1559.6	0.5486	1996.6	0.8522	1018.0
0.3130	1901.5	0.5939	1955.7	0.9063	684.5
0.3707	1982.4	0.6413	1858.9	0.9553	350.1
Propyl Ethanoate (1) + *tert*-Butyl Alcohol (2)					
0.0506	333.4	0.3870	1727.2	0.7062	1555.5
0.1059	666.3	0.4295	1803.7	0.7783	1307.0
0.1612	993.3	0.4677	1825.3	0.8559	945.8
0.2204	1256.6	0.5217	1835.4	0.9283	539.3
0.2796	1475.2	0.5786	1803.8		
0.3339	1622.9	0.6401	1713.7		
Propyl Propanoate (1) + *tert*-Butyl Alcohol (2)					
0.0452	273.6	0.4006	1652.6	0.6235	1660.0
0.1058	588.8	0.4527	1704.9	0.7205	1437.0
0.1761	932.9	0.4631	1719.7	0.8240	1045.5
0.2493	1250.0	0.5064	1728.9	0.9193	538.3
0.3205	1474.8	0.5370	1725.1		
0.3891	1629.9	0.5573	1724.7		
Propyl Butanoate (1) + *tert*-Butyl Alcohol (2)					
0.0342	193.8	0.2948	1359.9	0.5150	1693.6
0.0755	420.8	0.3409	1484.0	0.5782	1680.5
0.1160	636.4	0.3865	1574.8	0.6520	1583.5
0.1522	824.9	0.4067	1614.0	0.7324	1393.3
0.2039	1032.8	0.4282	1643.7	0.8229	1055.7
0.2539	1221.3	0.4571	1672.4	0.9118	592.6
318.15 K					
Propyl Methanoate (1) + *tert*-Butyl Alcohol (2)					
0.0560	413.0	0.4247	1915.9	0.7432	1534.1
0.1213	800.1	0.4661	1956.8	0.8096	1248.3
0.1861	1142.8	0.5122	1971.8	0.8771	875.9
0.2515	1421.9	0.5643	1947.8	0.9405	470.6
0.3123	1641.6	0.6206	1870.1		
0.3674	1790.9	0.6781	1740.1		
Propyl Ethanoate (1) + *tert*-Butyl Alcohol (2)					
0.0437	253.2	0.3804	1670.3	0.5704	1798.4
0.0939	520.6	0.4115	1737.3	0.6343	1714.7
0.1490	803.9	0.4179	1747.8	0.7055	1548.5
0.2040	1057.3	0.4562	1789.8	0.7756	1303.7
0.2592	1279.1	0.4638	1794.1	0.8554	937.2
0.3141	1489.6	0.4957	1815.6	0.9304	505.6
0.3611	1617.9	0.5115	1822.0		
Propyl Propanoate (1) + *tert*-Butyl Alcohol (2)					
0.0426	237.5	0.3964	1591.7	0.6467	1617.9
0.0877	477.8	0.4416	1674.4	0.7169	1450.9
0.1426	733.0	0.4831	1716.6	0.7848	1216.1
0.1958	968.6	0.5037	1723.5	0.8547	890.6
0.2492	1189.4	0.5223	1725.2	0.9376	453.1
0.2972	1343.8	0.5476	1719.8		
0.3488	1489.8	0.5960	1684.8		
Propyl Butanoate (1) + *tert*-Butyl Alcohol (2)					
0.0544	290.2	0.3867	1553.3	0.5988	1667.2
0.1126	578.9	0.4260	1625.3	0.6689	1560.8
0.1688	836.3	0.4292	1630.5	0.7436	1370.9
0.2307	1099.9	0.4640	1660.6	0.8141	1107.5
0.2881	1298.7	0.5016	1691.9	0.8864	761.9
0.3385	1434.3	0.5498	1687.9	0.9510	367.6

The form of this equation for a generic function (Y^{E}_{m}) is as follows:

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

where

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

and b_i are parameters that must be determined by a least-squares

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

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

binary mixture	k_v (k_r)	b_o	b_1	b_2	$10^9 \cdot s(V_m^E)/m^3 \cdot mol^{-1}$
		T = 303.15 K			
tert-butyl alcohol (2) +					
+ propyl methanoate (1)	0.970 (0.993)	4094	−3593	2843	4
+ propyl ethanoate (1)	0.820 (0.832)	2611	509	138	2
+ propyl propanoate (1)	0.716 (0.715)	1974	−157	1431	4
+ propyl butanoate (1)	0.634 (0628)	1544	547	1456	4
		T = 318.15 K			
tert-butyl alcohol (2) +					
+ propyl methanoate (1)	0.969 (0.993)	4205	−3834	3254	7
+ propyl ethanoate (1)	0.821 (0.832)	2842	−716	1565	6
+ propyl propanoate (1)	0.718 (0.715)	1536	553	1560	7
+ propyl butanoate (1)	0.635 (0.628)	1848	−981	3090	6

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

binary mixture	k_h (k_q)	b_0	b_1	b_2	$s(H_m^E)/J \cdot mol^{-1}$
		T = 299.15 K			
tert-butyl alcohol (2) +					
+ propyl methanoate (1)	0.962 (0.978)	8476.1	−1695.5	1819.9	8.4
+ propyl ethanoate (1)	0.826 (0.834)	6074.9	1449.8	1880.4	12.8
+ propyl propanoate (1)	0.726 (0.726)	4468.9	3488.9	1920.8	9.1
+ propyl butanoate (1)	0.647 (0.644)	4116.5	1953.9	5018.8	11.2
		T = 318.15 K			
tert-butyl alcohol (2) +					
+ propyl methanoate (1)	0.963 (0.978)	7074.4	1609.2	−133.6	9.8
+ propyl ethanoate (1)	0.827 (0.834)	4645.1	5533.9	−1103.6	8.7
+ propyl propanoate (1)	0.728 (0.726)	4065.4	3967.8	2039.8	8.6
+ propyl butanoate (1)	0.649 (0.649)	3814.4	2142.3	5420.5	12.9

method when directly correlating the values of (x_1, Y_m^E) for each of the mixtures studied. The k parameter can be obtained, either with the same data fitting procedure to achieve the best correlation or by first establishing it for a specific value depending on the amount to be represented. The dependence of k on pressure and temperature will be studied in depth in future works. In previous works,[1−3] it was proposed that in the correlations of excess volumes the equivalences of $k \equiv k_v = V_2^o/V_1^o$ can be established, where $V_i^o(T)$ are the molar volumes of the pure components of the mixture measured at the same working temperature of the amounts $Y_m^E = Y_m^E(x)$ (see Ortega et al.).[11] Similar results are obtained when k_v is estimated from the quotient of volume parameters and area obtained by weighting the values corresponding to each group, R_k and Q_k,

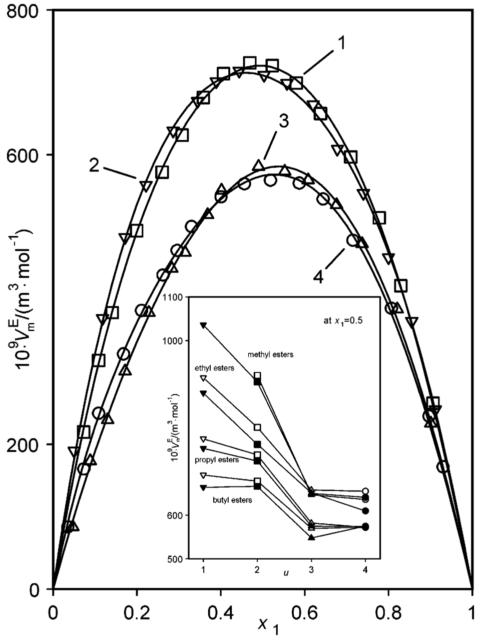

Figure 1. Experimental values and correlation curves, eq 1 (solid line), of V_m^E vs x_1 at 318.15 K for binary mixtures $C_{u-1}H_{2u-1}COO(CH_2)_2CH_3$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2). Labels indicate the u-values. Inset shows the variation of equimolar volumes as a function of u and temperature and comparison between the values for methyl, ethyl, propyl, and butyl esters; solid symbols at 303.15 K; open symbols at 318.15 K. ▽, for u = 1; □, for u = 2; △, for u = 3; ○, for u = 4.

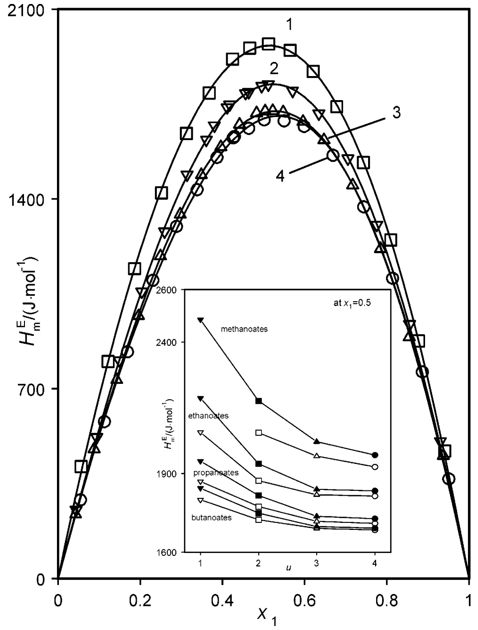

Figure 2. Experimental values and correlation curves, eq 1 (solid line), of H_m^E vs x_1 at 318.15 K for binary mixtures $C_{u-1}H_{2u-1}COO(CH_2)_{v-1}CH_3$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2). Labels indicate the u-values. Inset shows the variation of equimolar enthalpies as a function of v and temperature and comparison between the values for methanoates, ethanoates, propanoates, and butanoates; solid symbols at 299.15 K; open symbols at 318.15 K. ▽, for v = 1; □, for v = 2; △, for v = 3; ○, for v = 4.

Table 5. Experimental Vapor Pressures, p_i^o, for Propyl Esters as a Function of Temperature

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	T / K	p_i^o / kPa	T / K	p_i^o / kPa
Propyl Methanoate															
327.46	40.15	336.50	57.37	344.09	73.41	349.81	89.23	354.57	104.04	359.06	120.04	363.17	136.08	366.85	152.01
328.16	41.27	337.03	58.48	344.53	74.63	350.30	90.72	354.90	105.28	359.46	121.43	363.47	137.24	367.17	153.22
329.18	42.84	337.52	60.10	345.02	76.02	350.81	92.08	355.29	106.69	359.75	122.55	363.85	138.75	367.46	154.59
329.82	43.83	338.33	61.22	345.47	77.14	351.16	93.24	355.66	107.94	360.06	123.91	364.10	140.03	367.78	156.05
330.59	45.21	339.57	62.78	346.10	78.74	351.58	94.54	356.11	109.37	360.48	125.41	364.44	141.27	368.05	157.21
331.39	46.74	339.98	63.77	346.49	79.91	352.12	96.11	356.48	110.63	360.81	126.56	364.75	142.69	368.40	158.73
332.25	47.95	340.81	65.54	347.11	81.54	352.50	97.42	356.82	111.95	361.15	127.96	365.06	143.88	368.65	160.04
332.94	49.22	341.27	66.75	347.49	82.63	352.93	98.70	357.28	113.41	361.52	129.37	365.38	145.41	368.96	161.42
333.66	50.78	341.76	67.92	348.02	83.95	353.31	100.09	357.58	114.71	361.82	130.63	365.66	146.72	369.19	162.50
334.29	51.81	342.38	69.35	348.50	85.40	353.64	101.20	357.96	116.06	362.18	131.96	366.03	148.06		
335.07	53.22	343.04	70.87	348.91	86.62	353.76	101.32	358.33	117.23	362.55	133.55	366.30	149.41		
335.67	54.78	343.48	71.97	349.36	87.87	354.06	102.55	358.68	118.72	362.86	137.73	366.60	150.62		
Propyl Ethanoate															
346.36	39.93	356.00	56.06	363.46	72.01	369.62	88.02	375.06	104.06	379.86	120.04	384.08	136.05	387.98	151.97
347.24	41.38	356.66	57.35	364.07	73.37	370.10	89.26	375.48	105.27	380.17	121.35	384.40	137.37	388.27	153.32
348.26	42.70	357.26	58.73	364.61	74.69	370.67	90.71	375.89	106.69	380.59	122.71	384.75	138.63	388.54	154.58
349.06	43.97	357.90	60.02	365.08	74.94	371.05	92.01	376.24	107.91	380.95	123.93	385.10	139.99	388.92	156.05
349.83	45.25	358.62	61.37	365.61	77.29	371.50	93.22	376.66	109.23	381.24	125.23	385.42	141.25	389.18	157.37
350.70	46.70	359.26	62.63	366.18	78.71	371.96	94.56	377.13	110.71	381.58	126.55	385.77	142.72	389.48	158.71
351.50	47.91	359.91	63.95	366.74	80.02	372.42	95.92	377.47	112.02	381.95	127.93	386.07	143.94	389.75	159.92
352.27	49.26	360.48	65.35	367.17	81.41	372.91	97.22	377.91	113.29	382.35	129.43	386.37	145.34	390.07	161.33
353.04	50.82	361.07	66.74	367.62	82.62	373.36	98.72	378.34	114.72	382.67	130.53	386.70	146.57	390.34	162.57
353.86	82.01	361.64	68.02	368.22	84.03	373.80	100.02	378.67	116.04	383.00	131.85	387.06	148.02	390.68	163.96
354.40	53.30	362.32	69.41	368.71	85.34	374.17	101.32	379.06	117.24	383.34	133.24	387.31	149.25		
355.27	54.67	362.93	70.71	369.17	86.59	374.57	102.59	379.44	118.56	383.77	134.71	387.66	150.56		
Propyl Propanoate															
366.23	39.89	376.07	55.93	384.05	71.97	390.50	87.96	395.74	102.64	400.85	118.59	405.42	134.57	409.56	150.48
367.27	41.36	376.90	57.26	384.62	73.27	391.00	89.28	396.19	103.94	401.29	120.00	405.78	135.99	409.86	151.93
368.07	42.61	377.62	58.62	385.13	74.63	391.51	90.68	396.61	105.29	401.65	121.25	406.11	137.21	410.19	153.29
368.98	43.92	378.26	59.88	385.72	76.01	392.00	91.96	397.12	106.62	401.98	122.57	406.49	138.59	410.54	154.72
369.87	45.32	378.98	61.27	386.32	77.23	392.47	93.27	397.48	107.94	402.43	123.96	406.86	140.04	410.87	155.88
370.68	46.63	379.63	62.67	386.87	78.55	393.00	94.62	398.00	109.34	402.75	125.25	407.17	141.31	411.19	157.28
371.56	47.95	380.28	63.97	387.36	79.83	393.47	95.96	398.37	110.55	403.17	126.73	407.50	142.56	411.46	158.50
372.37	49.27	380.97	65.29	387.99	81.28	393.89	97.26	398.76	111.92	403.54	127.97	407.86	144.05	411.86	160.04
373.17	50.69	381.51	66.62	388.51	82.58	394.37	98.62	399.26	113.27	403.94	129.24	408.26	145.37	412.14	161.24
373.87	51.93	382.10	67.91	389.05	83.96	394.82	99.92	399.62	114.61	404.23	130.45	408.59	146.68	412.48	162.64
374.72	53.29	382.79	69.27	389.50	85.35	395.39	101.32	400.03	115.83	404.62	131.95	408.84	147.90	412.72	163.78
375.46	54.69	383.45	70.67	390.03	86.63	395.32	101.43	400.40	117.01	405.07	133.29	409.19	149.29		
Propyl Butanoate															
388.56	43.87	398.28	59.77	406.31	76.10	412.97	92.04	419.27	109.48	424.67	126.72	429.17	142.83	433.25	158.57
389.46	45.25	399.01	61.21	406.87	77.29	413.49	93.23	419.72	110.81	425.03	127.89	429.50	144.03	433.67	160.22
390.48	46.70	399.87	62.75	407.55	78.82	414.13	94.87	420.16	112.15	425.49	129.40	429.94	145.46	434.04	161.76
391.30	47.94	400.41	63.83	408.00	79.94	414.55	96.02	420.57	113.51	425.88	130.76	430.24	146.70		
392.02	49.13	401.24	65.43	408.69	81.52	416.09	100.22	421.03	114.80	426.24	132.19	430.60	148.16		
392.88	50.51	401.94	66.83	409.10	82.49	416.37	101.09	421.41	116.01	426.60	133.49	431.02	149.64		
393.72	51.81	402.48	67.94	409.69	83.91	416.41	101.32	421.88	117.53	426.99	134.84	431.33	150.89		
394.46	53.11	403.26	69.43	410.31	85.43	416.89	102.54	422.30	118.83	427.36	136.08	431.67	152.16		
395.34	54.57	403.72	70.41	410.74	86.46	417.45	104.08	422.73	120.27	427.74	137.52	431.99	153.50		
396.00	55.71	404.37	71.86	411.26	87.71	417.90	105.49	423.40	122.43	428.10	138.84	432.37	154.82		
396.93	57.26	405.16	73.41	411.87	89.22	418.38	106.89	423.77	123.91	428.41	139.92	432.62	156.09		
397.62	58.55	405.63	74.55	412.52	90.83	418.76	108.16	424.21	125.20	428.86	141.48	432.98	157.50		

of van der Waals (see Bondi),[12] determined, respectively, by $r_i = \sum_k \upsilon_k^{(i)} R_k$ and $q_i = \sum_k \upsilon_k^{(i)} Q_k$, where $\upsilon_k^{(i)}$ is the whole number corresponding to the number of k-type groups in a molecule of the i component. The quotients calculated for r_i and q_i are constant values for each mixture, independent of temperature and of structural changes in the compounds, as occurs in this study, in which the same results would be obtained for another butanol isomer. Table 4 shows slight differences between the values obtained with both procedures. However, for the aforementioned reasons, we prefer to use the method planning here.

To establish values of this parameter in the case of another property, such as enthalpies, the method does have the drawbacks mentioned above. However, if we consider there to be a direct relation between enthalpic effects and the contact surface between the molecules, we can obtain a surface/volume ratio, by assuming the molecules to be spherical, establishing a relationship with the surface and volume parameters given by Bondi.[12] This gives us the following expression for k_h, which is equivalent to k for the correlation of enthalpies:

$$k_h = \left(\frac{q_2}{q_1}\right)\left(\frac{V_{m,2}}{V_{m,1}}\right)^{2/3}\left(\frac{r_1}{r_2}\right)^{2/3} = \left(\frac{q_2}{q_1}\right)\left(\frac{k_v r_1}{r_2}\right)^{2/3} = k_q\left(\frac{k_v(T)}{k_r}\right)^{2/3} \quad (2)$$

producing in this way a weighted value for the quotient of surface parameters $k_q = q_2/q_1$, for the substances with factors that contain the quotient of volume parameters, $k_r = r_2/r_1$, and the quotient of real volumes, $k_v(T)$.

The pairs values correlations (x_1, V_m^E) and (x_1, H_m^E) shown in Tables 2 and 3 for the four binary systems studied here, using eq 1, produced the table of coefficients recorded in Table 4, by using a least-squares procedure, minimizing the standard devia-

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

compound	*A*	*B*	*C*	*ω* exp.; lit.	Δ*T*/K	ref
tert-butyl alcohol	6.60044	1238.69	85.99		330−370	ref 1
	(2.9984)	(2.4439)	(0.170)	0.614; 0.616[7]		ref 1
propyl methanoate	6.10108	1200.66	60.54		315−375	this work
	5.97008	1132.3	68.35			ref 6
	6.07030	1181.20	63.30		320−370	ref 13
	6.16037	1226.68	58.39		300−355	ref 15
	(2.4738)	(2.2119)	(0.1148)	0.306; 0.318[7]		this work
propyl ethanoate	6.49837	1514.82	37.03		335−400	this work
	6.14362	1284.08	64.36			ref 6
	6.51160	1524.56	36.19		320−430	ref 13
	6.07167	1240.55	69.10		330−370	ref 15
	(2.9715)	(2.7572)	(0.067)	0.387; 0.394[7]		this work
propyl propanoate	6.03936	1287.02	76.26		355−420	this work
	6.06539	1301.06	75.11		360−420	ref 13
	6.19565	1383.66	65.07		330−395	ref 15
	(2.5469)	(2.2269)	(0.132)	0.373; 0.376[7]		this work
propyl butanoate	6.62934	1772.82	33.00		380−444	this work
	6.60941	1723.42	42.02		375−440	ref 13
	6.32482	1543.16	59.45		350−420	ref 15
	(3.1708)	(2.9700)	(0.057)	0.449; 0.448[7]		this work

[a] Given in parentheses are the coefficients *a*, *b*, and *c* of the Antoine equation in reduced form, $\log(p^{\mathrm{o}}_{i,\mathrm{r}}) = a - b/(T_{\mathrm{r}} - c)$.

tion $s(Y^{\mathrm{E}}_{\mathrm{m}})$ of the data for each mixture, which are also compiled in this table. The set of experimental data of volumes and enthalpies and their corresponding correlations are shown graphically in Figures 1 and 2 at a temperature of 318.15 K. To avoid confusion, values obtained for $V^{\mathrm{E}}_{\mathrm{m}}$ and for $H^{\mathrm{E}}_{\mathrm{m}}$ at other temperatures have not been included. This is because there are only minimal differences between them, as can be observed in the insets, which show the change in equimolar quantities with the acid (methanoate to butanoate) and alkanolic chains (methyl, propyl, and butyl) and temperature. In Figure 1, it can be deduced that the volumes for the mixtures (propyl esters + *tert*-butyl alcohol) are positive and decrease with increased chain length of the propyl ester, following a quasi-identical variation to that observed with similar systems,[1−3] which can be observed in the corresponding inset. The quantity $(\partial V^{\mathrm{E}}_{\mathrm{m}}/\partial T)_{p,x}$ is also positive for systems of methanoate to propanoate (methyl to propyl), but the tendency becomes slightly opposite in the butyl esters. Analogously, Figure 2 shows the excess enthalpies with endothermic effects in all cases, while the corresponding inset shows the variation in equimolar volume with temperature and the number of carbons in the alkanolic part of the alkyl esters. Here, the results corresponding to the other mixtures studied in previous works have been included.[1−3] In this case, the quantity $(\partial H^{\mathrm{E}}_{\mathrm{m}}/\partial T)_{p,x}$ is negative for all the four systems studied, decreasing the $H^{\mathrm{E}}_{\mathrm{m}}(T)$ slope with increasing ester chain length, both in its acid part and in its alkanoic part.

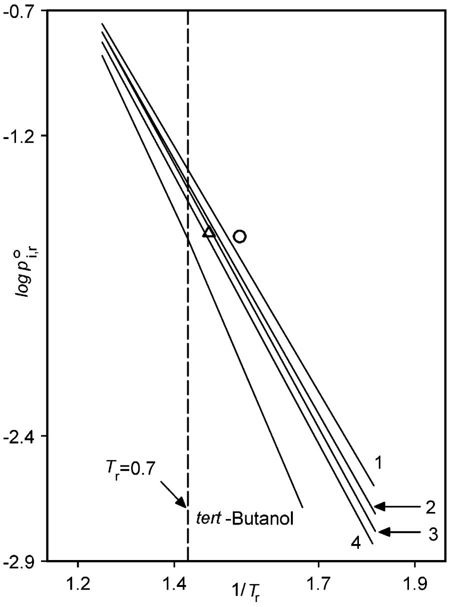

Figure 3. Vapor pressures lines in reduced coordinates for propyl esters $C_{u-1}H_{2u-1}COO(CH_2)_2\ CH_3$ and *tert*-butyl alcohol calculated using the coefficients of Table 6. Labels indicate the *u*-values. $T_{\mathrm{r}} = T/T_{\mathrm{c}}$ and $p_{\mathrm{r}} = p/p_{\mathrm{c}}$. Situation of azeotropic point in reduced coordinates for the binary (propyl methanoate + *tert*-butyl alcohol) (○, this work) and for (ethyl ethanoate + *tert*-butyl alcohol) (△, ref 2).

Vapor Pressures. Owing to the influence of vapor pressure data (p^{o}_i) or its correlations on the quantities that characterize isobaric VLE, it is common practice for our team to experimentally determine the pairs (T, p^{o}_i) for the substances used. The purpose of this is to try to cover the widest range of pressures and temperatures possible with the continually updated VLE experimental apparatus. The vapor pressures of *tert*-butyl alcohol were presented in a previous paper,[1] and those corresponding to the four propyl esters (methanoate to butanoate) were obtained in our laboratory years ago.[13] It was decided to make new measurements for the propyl esters using the same equilibrium apparatus but trying to increase the temperature interval, taking into consideration in all cases the limitations posed by using a glass ebullometer. The experimental results of p^{o}_i versus T for the propyl esters are shown in Table 5 and were correlated with Antoine's well-known equation:

$$\log(p^{\mathrm{o}}_i/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) - C] \qquad (3)$$

where the constants *A*, *B*, and *C* were determined by a least-squares method (see Table 6), minimizing the standard deviation of the pressure data $s(p^{\mathrm{o}}_i)$. In this table, the values obtained are compared with those found in the literature[13−15] and showed a good degree of similarity. The correlation obtained in this way is required to characterize the VLE of these mixtures. The vapor pressure lines for the pure compounds used (propyl esters and *tert*-butyl alcohol) have been shown in Figure 3 using reduced coordinates for pressure and temperature. Now, the pairs (T_{r}, $p^{\mathrm{o}}_{i,\mathrm{r}}$) in their reduced form have been correlated for each substance with a similar expression to eq 3, $\log p^{\mathrm{o}}_{i,\mathrm{r}} = a - b/$

Table 7. Experimental Data, $T-x_1-y_1$, and Calculated Quantities for the VLE of the Binary Mixtures of Propyl Ester (1) + *tert*-Butyl Alcohol (2) at 101.32 kPa

T/K	x_1	y_1	γ_1	γ_2	G^E_m/RT	T/K	x_1	y_1	γ_1	γ_2	G^E_m/RT
Propyl Methanoate (1) + *tert*-Butyl Alcohol (2)											
354.61	0.0251	0.0409	1.601	1.020	0.031	350.53	0.5826	0.5973	1.134	1.175	0.141
354.47	0.0339	0.0548	1.595	1.020	0.035	350.52	0.6223	0.6267	1.114	1.205	0.138
354.27	0.0424	0.0680	1.592	1.022	0.041	350.51	0.6509	0.6475	1.101	1.232	0.135
354.01	0.0599	0.0942	1.573	1.022	0.048	350.63	0.6832	0.6731	1.086	1.254	0.128
353.59	0.0895	0.1382	1.563	1.021	0.058	350.69	0.7095	0.6944	1.076	1.276	0.123
353.17	0.1153	0.1715	1.525	1.026	0.072	350.79	0.7366	0.7168	1.066	1.299	0.116
353.12	0.1217	0.1808	1.525	1.024	0.072	350.90	0.7586	0.7333	1.056	1.329	0.109
352.75	0.1520	0.2180	1.488	1.027	0.083	350.96	0.7743	0.7458	1.049	1.353	0.106
352.47	0.1799	0.2535	1.474	1.025	0.090	351.00	0.7816	0.7518	1.047	1.363	0.103
352.27	0.1964	0.2707	1.450	1.030	0.097	351.30	0.8201	0.7876	1.035	1.400	0.089
352.06	0.2233	0.2971	1.409	1.036	0.104	351.46	0.8353	0.8024	1.030	1.415	0.082
351.67	0.2684	0.3421	1.365	1.045	0.116	351.86	0.8754	0.8425	1.019	1.469	0.065
351.31	0.3284	0.3942	1.299	1.063	0.127	352.10	0.8988	0.8670	1.014	1.514	0.054
351.04	0.3840	0.4423	1.256	1.079	0.134	352.32	0.9117	0.8816	1.009	1.532	0.046
350.91	0.4104	0.4642	1.238	1.089	0.138	352.63	0.9437	0.9183	1.006	1.639	0.034
350.77	0.4526	0.4976	1.208	1.106	0.141	352.90	0.9624	0.9417	1.003	1.734	0.024
350.65	0.4955	0.5321	1.184	1.124	0.143	352.97	0.9692	0.9503	1.003	1.800	0.021
350.56	0.5427	0.5669	1.155	1.152	0.143						
Propyl Ethanoate (1) + *tert*-Butyl Alcohol (2)											
355.88	0.0601	0.0492	1.459	1.000	0.023	362.40	0.6172	0.4524	1.051	1.118	0.073
356.02	0.0859	0.0695	1.435	1.001	0.032	363.05	0.6493	0.4825	1.044	1.127	0.070
356.21	0.1183	0.0944	1.406	1.003	0.043	364.15	0.6970	0.5319	1.035	1.136	0.063
356.47	0.1557	0.1203	1.349	1.008	0.053	364.95	0.7302	0.5687	1.030	1.143	0.058
356.87	0.2030	0.1529	1.296	1.013	0.063	365.68	0.7591	0.6033	1.028	1.148	0.054
357.18	0.2424	0.1791	1.258	1.021	0.072	366.67	0.7938	0.6485	1.024	1.149	0.047
357.53	0.2796	0.2024	1.218	1.030	0.076	367.24	0.8127	0.6741	1.022	1.151	0.044
357.85	0.3053	0.2189	1.194	1.034	0.077	367.33	0.8153	0.6770	1.020	1.153	0.043
358.32	0.3494	0.2476	1.161	1.046	0.081	367.67	0.8265	0.6927	1.019	1.154	0.040
358.77	0.3858	0.2723	1.140	1.054	0.083	369.12	0.8721	0.7625	1.017	1.153	0.033
359.25	0.4255	0.2997	1.119	1.066	0.084	369.97	0.8971	0.8032	1.015	1.155	0.028
359.58	0.4488	0.3153	1.104	1.073	0.083	370.56	0.9127	0.8307	1.014	1.148	0.025
360.01	0.4797	0.3389	1.095	1.081	0.084	371.51	0.9375	0.8748	1.010	1.150	0.018
360.49	0.5078	0.3602	1.082	1.087	0.081	372.47	0.9623	0.9222	1.008	1.148	0.013
361.12	0.5474	0.3903	1.066	1.101	0.078	373.23	0.9806	0.9592	1.007	1.142	0.009
361.63	0.5753	0.4147	1.058	1.107	0.076						
Propyl Propanoate (1) + *tert*-Butyl Alcohol (2)											
355.92	0.0207	0.0087	1.495	0.999	0.008	373.87	0.7223	0.3917	1.031	1.158	0.063
356.13	0.0347	0.0142	1.444	1.000	0.013	374.69	0.7391	0.4110	1.030	1.163	0.061
357.05	0.0884	0.0348	1.342	1.002	0.028	376.49	0.7739	0.4525	1.022	1.176	0.054
357.91	0.1384	0.0539	1.286	1.007	0.041	377.60	0.7944	0.4809	1.022	1.186	0.052
358.77	0.1864	0.0727	1.248	1.013	0.052	378.45	0.8075	0.5009	1.020	1.185	0.048
359.73	0.2368	0.0931	1.214	1.020	0.061	378.89	0.8145	0.5119	1.019	1.187	0.047
360.66	0.2835	0.1122	1.182	1.028	0.068	380.14	0.8361	0.5449	1.016	1.205	0.044
361.66	0.3311	0.1331	1.158	1.038	0.074	381.12	0.8504	0.5701	1.014	1.210	0.041
362.37	0.3638	0.1477	1.141	1.046	0.077	382.70	0.8722	0.6123	1.012	1.217	0.036
363.41	0.4106	0.1688	1.113	1.061	0.079	383.91	0.8877	0.6457	1.011	1.221	0.032
364.35	0.4476	0.1883	1.102	1.070	0.081	385.47	0.9074	0.6914	1.011	1.231	0.029
365.97	0.5072	0.2214	1.081	1.088	0.081	387.09	0.9246	0.7372	1.008	1.228	0.023
367.36	0.5549	0.2502	1.065	1.106	0.080	388.37	0.9379	0.7754	1.007	1.228	0.019
368.77	0.5955	0.2797	1.057	1.115	0.077	390.02	0.9548	0.8262	1.005	1.245	0.015
370.40	0.6422	0.3150	1.046	1.135	0.074	391.54	0.9692	0.8767	1.006	1.242	0.012
371.51	0.6721	0.3404	1.041	1.149	0.072	393.08	0.9828	0.9277	1.005	1.249	0.009
372.48	0.6925	0.3608	1.037	1.150	0.068	394.54	0.9946	0.9765	1.004	1.242	0.005
373.31	0.7107	0.3791	1.033	1.156	0.065						
Propyl Butanoate (1) + *tert*-Butyl Alcohol (2)											
355.90	0.0147	0.0030	1.409	1.000	0.005	366.26	0.4285	0.1018	1.115	1.071	0.086
356.40	0.0381	0.0078	1.386	1.000	0.013	367.94	0.4732	0.1178	1.100	1.077	0.084
356.89	0.0631	0.0130	1.369	1.003	0.023	368.56	0.4962	0.1247	1.087	1.095	0.087
357.77	0.0997	0.0205	1.321	1.003	0.031	369.17	0.5109	0.1308	1.083	1.097	0.086
358.44	0.1295	0.0269	1.301	1.006	0.039	370.06	0.5358	0.1406	1.076	1.109	0.087
359.32	0.1675	0.0344	1.244	1.010	0.045	372.96	0.6001	0.1714	1.059	1.128	0.082
360.04	0.2009	0.0410	1.218	1.018	0.054	375.93	0.6615	0.2078	1.053	1.157	0.083
361.26	0.2488	0.0521	1.180	1.025	0.059	378.23	0.6997	0.2353	1.043	1.171	0.077
362.67	0.3071	0.0662	1.153	1.041	0.071	380.38	0.7332	0.2632	1.037	1.188	0.073
363.98	0.3523	0.0782	1.132	1.050	0.075	383.00	0.7695	0.3005	1.036	1.205	0.070
365.37	0.4004	0.0928	1.123	1.063	0.083	385.49	0.7986	0.3357	1.029	1.216	0.063
365.72	0.4095	0.0958	1.119	1.063	0.082	388.51	0.8321	0.3839	1.027	1.238	0.058

Table 7 (Continued)

T/K	x_1	y_1	γ_1	γ_2	G^E_m/RT	T/K	x_1	y_1	γ_1	γ_2	G^E_m/RT
Propyl Butanoate (1) + *tert*-Butyl Alcohol (2)											
391.02	0.8553	0.4249	1.023	1.248	0.052	402.71	0.9375	0.6548	1.017	1.264	0.031
393.36	0.8761	0.4676	1.024	1.264	0.049	403.78	0.9442	0.6781	1.015	1.285	0.028
395.70	0.8933	0.5085	1.018	1.269	0.041	405.01	0.9504	0.7055	1.013	1.281	0.024
396.81	0.9005	0.5325	1.023	1.257	0.043	405.83	0.9549	0.7233	1.010	1.297	0.021
398.02	0.9097	0.5561	1.020	1.273	0.040	406.81	0.9602	0.7488	1.012	1.302	0.022
400.58	0.9248	0.6076	1.017	1.262	0.033	409.25	0.9702	0.8052	1.006	1.269	0.013
401.76	0.9325	0.6348	1.019	1.269	0.033	411.38	0.9806	0.8613	1.005	1.318	0.010
402.625	0.9379	0.6508	1.013	1.290	0.028	412.76	0.9859	0.8948	1.000	1.331	0.005

($T_r - c$), also reflecting parameters *a*, *b*, and *c* in Table 6. These coefficients could have been calculated from those included in Antoine's equation; since $c = C/T_c$, $b = B/T_c$ and $a = b/(1 - c)$ (see Ortega et al.).[14] However, these equations are obtained at a specific boundary conditions at the critical point, which are not always fulfilled owing to the limitations of Antoine's equation. It is, therefore, often recommendable to establish independent correlations of vapor pressure for reduced coordinates. Then, reliable values of acentric factors can be obtained, which can be calculated using Pitzer's definition, where $\omega = -(\log p^{o}_{i,r})_{T_r=0.7} - 1$. In this case, the values obtained, which were used afterward to characterize VLE data, were compared with data in the literature and those estimated by the empirical procedure of Lee−Kesler and gave similar and acceptable values in all cases.

Presentation of VLE Data. The values obtained directly (p, T, x_1, y_1) in the isobaric VLE experimentation at a pressure

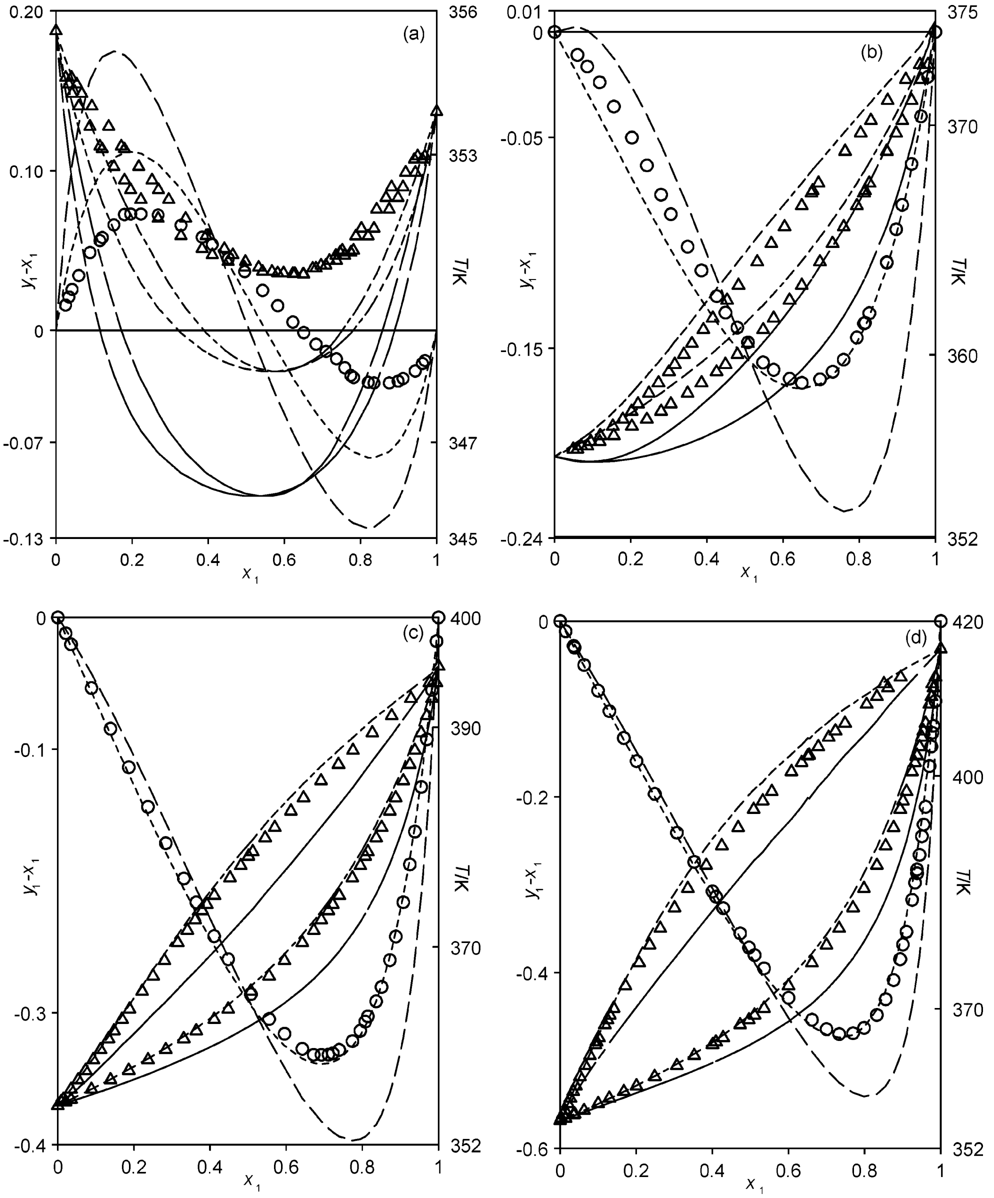

Figure 4. (a−d) Representation of VLE experimental values, ($y_1 - x_1$) vs x_1 (○) and T vs x_1, y_1 (△) for binary mixtures $C_{u-1}H_{2u-1}COO(CH_2)_2CH_3$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2). (a) for u = 1; (b) for u = 2; (c) for u = 3; (d) for u = 4. Dashed lines represent the curves estimated with the UNIFAC model: − −, Hansen et al.;[4] - - -, Gmehling et al.[5]

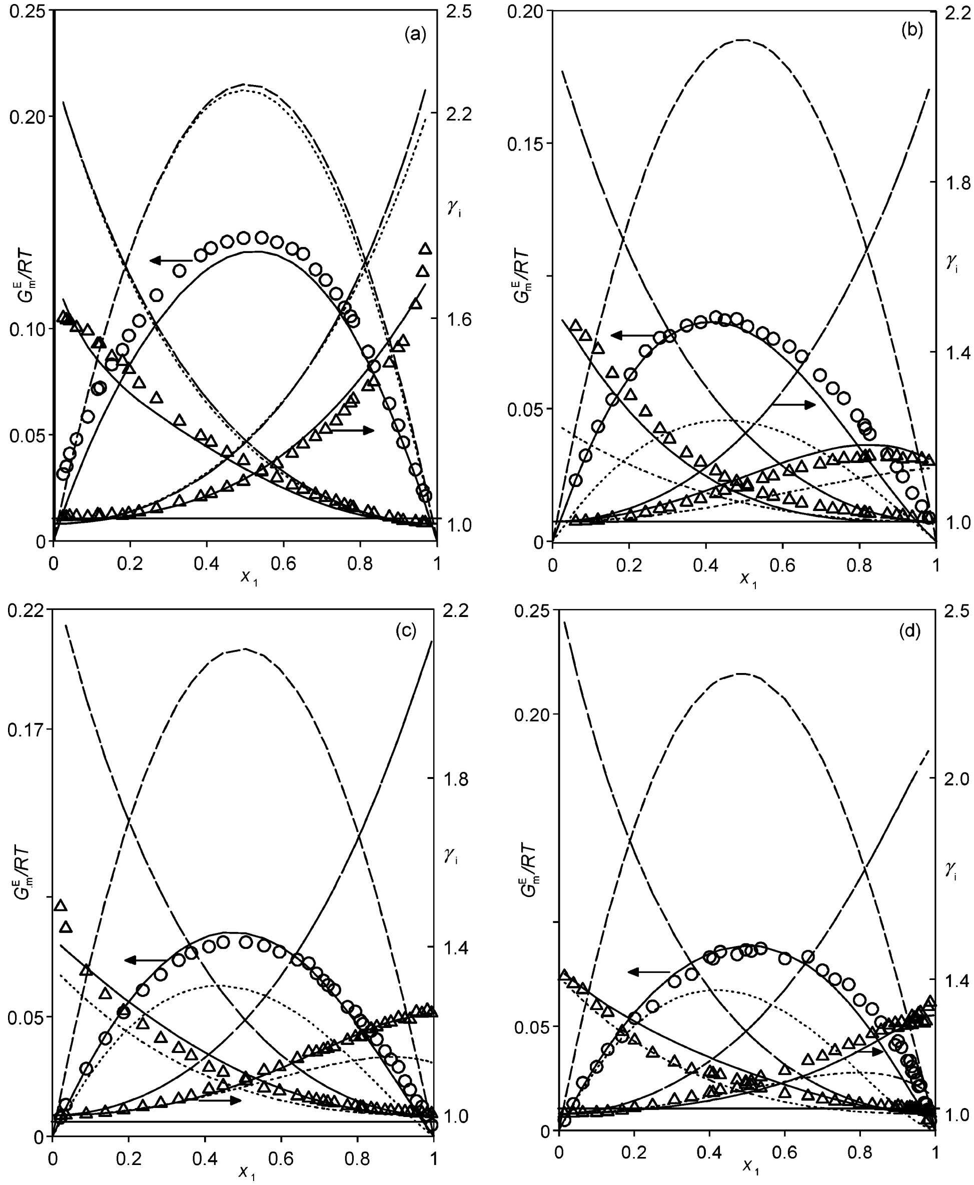

Figure 5. (a−d). Representation of experimental and correlated curves (—) for the quantities G^E_m/RT vs x_1 (○), and γ_i vs x_1 (△) for the binary mixtures $C_{u-1}H_{2u-1}COO(CH_2)_2CH_3$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2). (a) for $u = 1$; (b) for $u = 2$; (c) for $u = 3$; (d) for $u = 4$. Dashed lines represent the values estimated by the UNIFAC model: — —, Hansen et al.;[4] - - -, Gmehling et al.[5]

$p = (101.32 \pm 0.02)$ kPa, for the four binary mixtures of $\{x_1$ propyl esters (methanoate to butanoate) + $(1 - x_1)$*tert*-butyl alcohol$\}$ are compiled in Table 7. From these, taking into account the non-ideal nature of the vapor phase, the activity coefficients of the components in the liquid phase are calculated by

$$\ln \gamma_i = \ln\left(\frac{p y_i}{p_i^o x_i}\right) + \frac{(B_{ii} - V_i^o)(p - p_i^o)}{RT} + \frac{p}{RT}(1 - y_i)^2 \delta_{ij} \quad (4)$$

where $\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$ and where the second virial coefficients, for both pure B_{ii} compounds and for the mixtures B_{ij}, are calculated using the correlations proposed by Tsonopoulos.[16,17] The molar volumes in saturation V_i^o of each pure component i at each equilibrium temperature is obtained in a approximated form by the Rackett equation as modified by Spencer and Danner,[18] using the values for the Z_{RA} coefficient recorded in Reid et al.[19] With the activity coefficients shown in Table 7, calculated with eq 4, values for the adimensional Gibbs function $G^E_m/RT = \sum x_i \ln \gamma_i$ are obtained, which are also presented in Table 7 at each concentration and for each binary system. The version of the point-to-point consistency test proposed by Fredenslund at al.[20] was applied to all the mixtures, and in all cases the average differences between the molar fractions of the vapor phase, experimental values, and those calculated by the method, $\bar{\delta} = \sum_i (y_{i,\text{exp}} - y_{i,\text{cal}})/N$, verified the global condition stablished for the method, $\bar{\delta} \leq 0.01$, for all mixtures.

Figure 4a−d shows the quantities of T versus x_1, y_1 and $(y_1 - x_1)$ versus x_1 for the four systems of propyl esters (1) + *tert*-butyl alcohol (2). As indicated in the Introduction, the literature does not report VLE data for the systems studied here that can be used for comparison. The binary system $\{x_1$ propyl methanoate + $(1 - x_1)$*tert*-butyl alcohol$\}$ presents an azeotropic point at the following coordinates, $x_{1,\text{az}} = 0.621$, $T_{\text{az}} = 350.52$ K, which has been included in the diagram of vapor pressure lines in Figure 3. Reduced coordinates are also used, applying the corresponding geometric means of the critical properties of

Table 8. Results Obtained in the Correlation and Prediction of VLE and Excess Enthalpies of the Binary Mixtures Propyl Alkanoate (1) + *tert*-Butyl Alcohol (2) Using Different Models and Standard Deviation for the Quantity *Y*, *s*(*Y*)[a]

	UNIQUAC	Wilson	NRTL	eq 8		UNIFAC[b]	UNIFAC[c]
Propyl Methanoate (1) + *tert*-Butyl Alcohol (2)							
	$\Delta u_{12} = 779.14$	$\Delta\lambda_{12} = 309.06$	$\Delta g_{12} = 19820.27$	$A_{00} = 735.18$	$A_{01} = 737.51$		
	$\Delta u_{21} = -215.07$	$\Delta\lambda_{21} = 1425.92$	$\Delta g_{21} = -23204.75$	$A_{20} = -1.700$	$A_{21} = -1.630$		
			$\alpha = -0.0316$		$k = 0.674$		
$s(Q)$	0.012 (0.93)	0.012 (0.93)	0.012 (0.93)		0.011 (0.94)	0.045 (0.73)	0.043 (0.74)
$s(\gamma)$	0.028 (0.98)	0.028 (0.98)	0.037 (0.97)		0.034 (0.98)	0.264 (0.74)	0.250 (0.75)
$s(H^E_m)$	1283.3 (0.47)	1283.6 (0.47)	56.3 (0.99)		54.0 (0.99)		370.8 (0.66)
Propyl Ethanoate (1) + *tert*-Butyl Alcohol (2)							
	$\Delta u_{12} = -1060.43$	$\Delta\lambda_{12} = 2415.66$	$\Delta g_{12} = -17004.40$	$A_{00} = 778.88$	$A_{01} = 336.26$		
	$\Delta u_{21} = 1664.82$	$\Delta\lambda_{21} = -686.70$	$\Delta g_{21} = 13203.09$	$A_{20} = -1.818$	$A_{21} = -1.018$		
			$\alpha = -0.0627$		$k = 0.886$		
$s(Q)$	0.008 (0.90)	0.008 (0.90)	0.009 (0.92)		0.007 (0.94)	0.077 (0.57)	0.028 (0.63)
$s(\gamma)$	0.041 (0.85)	0.040 (0.86)	0.031 (0.93)		0.023 (0.95)	0.312 (0.59)	0.076 (0.77)
$s(H^E_m)$	974.0 (0.47)	1360.3 (0.47)	52.6 (0.99)		37.5 (0.99)		245.8 (0.78)
Propyl Propanoate (1) + *tert*-Butyl Alcohol (2)							
	$\Delta u_{12} = -86.36$	$\Delta\lambda_{12} = 885.28$	$\Delta g_{12} = -16358.91$	$A_{00} = 875.61$	$A_{01} = -177.97$		
	$\Delta u_{21} = 411.05$	$\Delta\lambda_{21} = 365.80$	$\Delta g_{21} = 13332.92$	$A_{20} = -2.046$	$A_{21} = 0.458$		
			$\alpha = -0.057$		$k = 1.190$		
$s(Q)$	0.007 (0.94)	0.007 (0.94)	0.011 (0.90)		0.004 (0.98)	0.081 (0.58)	0.016 (0.70)
$s(\gamma)$	0.013 (0.99)	0.012 (0.99)	0.040 (0.91)		0.017 (0.97)	0.373 (0.60)	0.052 (0.73)
$s(H^E_m)$	1158.3 (0.47)	1171.9 (0.47)	50.9 (0.98)		21.0 (0.99)		336.8 (0.66)
Propyl Butanoate (1) + *tert*-Butyl Alcohol (2)							
	$\Delta u_{12} = 1012.35$	$\Delta\lambda_{12} = -563.28$	$\Delta g_{12} = 12072.63$	$A_{00} = 822.39$	$A_{01} = -35.11$		
	$\Delta u_{21} = -562.05$	$\Delta\lambda_{21} = 1618.71$	$\Delta g_{21} = -15031.11$	$A_{20} = -1.907$	$A_{21} = 0.242$		
			$\alpha = -0.0675$		$k = 1.136$		
$s(Q)$	0.010 (0.88)	0.010 (0.88)	0.009 (0.93)		0.008 (0.94)	0.080 (0.60)	0.023 (0.66)
$s(\gamma)$	0.012 (0.99)	0.012 (0.99)	0.025 (0.96)		0.025 (0.96)	0.426 (0.60)	0.089 (0.77)
$s(H^E_m)$	1155.6 (0.47)	1117.2 (0.47)	105.7 (0.95)		16.8 (0.99)		320.0 (0.67)

[a] $Q = G^E_m/RT$. $s(\gamma)$ is global standard deviation for two activity coefficients. Between parentheses is the corresponding goodness of fit, r^2. [b] Ref 4. [c] Ref 5.

the pure substances as a mixing rule for the pseudocritical quantities. Figure 5a−d displays the values of Gibbs function and the activity coefficients of the compounds that constitute each of these mixtures.

Treatment of VLE Data

To correlate VLE data, a model was used for Gibbs function, $G^E_m = G^E_m(x, T)$, which has been described in a simplified form in previous works.[1−3] Basically, the mathematical thermodynamic procedure consists of using a similar expression to that recorded in eq 1 to relate the Gibbs function and the concentration x, through the so-called active fraction of the quantity or dependent function z, while temperature dependency is included in the coefficients b_i. Equation 1 takes the following form:

$$\frac{G^E_m(x, T)}{RT} = z(1 - z)\sum_{i=0}^{m} b_i(T)z^i \qquad (5)$$

where z is defined as eq 1 to establish the dependence $z = z(x)$. The functional form of dependence of the b_i coefficients with temperature is based on the relationships of the Gibbs function with the mixing enthalpy. Hence, these coefficients are written as follows:

$$b_i(T) = a_{i1} \ln T + \frac{a_{i2}}{T} + a_{i3} \qquad (6)$$

and a slight simplification is introduced in which the natural logarithm of T is substituted by an equivalent expression; eq 6 is reduced to $b_i(T) = (A_{i1}/T) + A_{i2}$. Now, a simultaneous correlation of data in Table 7 could be carried out, of $G^E_m(x, T)$ and the values of $H^E_m(x, T)$ recorded in Table 3, and considering that

$$\frac{H^E_m(x, T)}{RT} = -T\left[\frac{\partial(G^E_m/RT))}{\partial T}\right]_{p,x} = T\left[z(1 - z)\sum_{i=0}^{m}\left(\frac{A_{i1}}{T}\right)z^i\right] \qquad (7)$$

However, there are two important questions that arise when applying the model to specific cases, both of which are related to optimizing the mathematical treatment. The former refers to the unnecessary over-parametrization of the model proposed, both in ref 5 and in ref 7, suggesting simplification of the polynomial in brackets that weights the product $z(1 - z)$. Hence, in most cases it is sufficient to only consider two addenda, the independent term (b_0) and the term in z^2 (b_2). Now, the final expression of the model used for the Gibbs function and for the enthalpy becomes

$$\frac{G^E_m}{RT} = z(1 - z)\left[\left(\frac{A_{00}}{T} + A_{01}\right) + \left(\frac{A_{20}}{T} + A_{21}\right)z^2\right] \qquad (8)$$

$$\frac{H^E_m}{RT^2} = z(1 - z)\left[\left(\frac{A_{00}}{T^2}\right) + \left(\frac{A_{20}}{T^2}\right)z^2\right] \qquad (9)$$

The second question to take into account is the objective function. As a criterion of discrepancy between theoretical and experimental values to establish the objective function, it was considered to be more suitable to use values of enthalpies and activity coefficients because these are experimental values obtained more directly. Since values of the Gibbs function are calculated from the activity coefficients (γ_i), it is best to use the values obtained directly from eq 4, since the values of the

Table 9. Goodness of Fit Parameters, r^2, and Standard Deviation, *s*, Obtained in Application of Correlation and Prediction Models to Alkyl Esters (1) + *tert*-Butyl Alcohol (2) Mixtures[a]

	UNIQUAC	Wilson	NRTL	eq 8	UNIFAC[b]	UNIFAC[c]
			Methyl Methanoate (1) + *tert*-Butyl Alcohol (2)[d]			
$s(Q)$	0.015 (0.91)	0.015 (0.91)	0.030 (0.79)	0.004 (0.99)	0.009 (0.61)	0.123 (0.58)
$s(\gamma)$	0.032 (0.98)	0.032 (0.98)	0.090 (0.87)	0.025 (0.98)	0.362 (0.70)	0.583 (0.63)
$s(H^{\mathrm{E}}_{\mathrm{m}})$	1589.8 (0.46)	1398.4 (0.47)	178.9 (0.93)	25.0 (0.99)		420.6 (0.69)
			Methyl Ethanoate (1) + *tert*-Butyl Alcohol (2)[d]			
$s(Q)$	0.005 (0.98)	0.005 (0.98)	0.024 (0.81)	0.004 (0.99)	0.060 (0.63)	0.019 (0.73)
$s(\gamma)$	0.012 (0.99)	0.012 (0.99)	0.090 (0.86)	0.024 (0.98)	0.218 (0.74)	0.086 (0.88)
$s(H^{\mathrm{E}}_{\mathrm{m}})$	1413.1 (0.47)	1407.8 (0.47)	171.1 (0.92)	84.5 (0.98)		212.8 (0.87)
			Methyl Propanoate (1) + *tert*-Butyl Alcohol (2)[d]			
$s(Q)$	0.008 (0.92)	0.008 (0.92)	0.013 (0.88)	0.005 (0.97)	0.051 (0.64)	0.017 (0.69)
$s(\gamma)$	0.019 (0.98)	0.020 (0.98)	0.043 (0.93)	0.013 (0.99)	0.222 (0.69)	0.049 (0.83)
$s(H^{\mathrm{E}}_{\mathrm{m}})$	1466.2 (0.47)	1379.0 (0.47)	109.4 (0.95)	39.8 (0.99)		385.3 (0.66)
			Methyl Butanoate (1) + *tert*-Butyl Alcohol (2)[d]			
$s(Q)$	0.005 (0.96)	0.005 (0.96)	0.014 (0.84)	0.003 (0.98)	0.068 (0.60)	0.018 (0.74)
$s(\gamma)$	0.015 (0.99)	0.016 (0.99)	0.051 (0.90)	0.016 (0.98)	0.280 (0.72)	0.074 (0.83)
$s(H^{\mathrm{E}}_{\mathrm{m}})$	1284.4 (0.47)	1252.9 (0.47)	141.0 (0.92)	81.6 (0.98)		383.2 (0.64)
			Ethyl Methanoate (1) + *tert*-Butyl Alcohol (2)[e]			
$s(Q)$	0.007 (0.98)	0.007 (0.97)	0.016 (0.90)	0.007 (0.98)	0.059 (0.68)	0.073 (0.65)
$s(\gamma)$	0.024 (0.99)	0.024 (0.99)	0.060 (0.93)	0.037 (0.98)	0.280 (0.72)	0.357 (0.68)
$s(H^{\mathrm{E}}_{\mathrm{m}})$	1396.2 (0.47)	1402.4 (0.47)	94.3 (0.97)	56.6 (0.99)		374.9 (0.70)
			Ethyl Ethanoate (1) + *tert*-Butyl Alcohol (2)[e]			
$s(Q)$	0.003 (0.98)	0.003 (0.98)	0.015 (0.86)	0.002 (0.98)	0.069 (0.59)	0.021 (0.58)
$s(\gamma)$	0.005 (0.99)	0.005 (0.99)	0.077 (0.81)	0.005 (0.99)	0.288 (0.60)	0.062 (0.86)
$s(H^{\mathrm{E}}_{\mathrm{m}})$	1393.2 (0.47)	1346.9 (0.47)	151.3 (0.92)	33.4 (0.99)		207.5 (0.84)
			Ethyl Propanoate (1) + *tert*-Butyl Alcohol (2)[e]			
$s(Q)$	0.006 (0.94)	0.006 (0.94)	0.008 (0.93)	0.004 (0.97)	0.077 (0.58)	0.017 (0.67)
$s(\gamma)$	0.020 (0.96)	0.020 (0.96)	0.056 (0.82)	0.011 (0.99)	0.283 (0.62)	0.038 (0.87)
$s(H^{\mathrm{E}}_{\mathrm{m}})$	1213.0 (0.47)	1218.1 (0.47)	115.0 (0.94)	32.0 (0.99)		351.5 (0.65)
			Ethyl Butanoate (1) + *tert*-Butyl Alcohol (2)[e]			
$s(Q)$	0.004 (0.99)	0.004 (0.99)	0.008 (0.96)	0.005 (0.98)	0.063 (0.64)	0.029 (0.76)
$s(\gamma)$	0.013 (0.99)	0.013 (0.99)	0.034 (0.96)	0.013 (0.99)	0.315 (0.68)	0.133 (0.76)
$s(H^{\mathrm{E}}_{\mathrm{m}})$	1192.2 (0.47)	1145.6 (0.47)	182.2 (0.86)	22.9 (0.99)		341.0 (0.66)
			Butyl Methanoate (1) + *tert*-Butyl Alcohol (2)[f]			
$s(Q)$	0.015 (0.83)	0.015 (0.83)	0.011 (0.92)	0.013 (0.98)	0.070 (0.62)	0.054 (0.67)
$s(\gamma)$	0.028 (0.96)	0.026 (0.97)	0.037 (0.94)	0.015 (0.99)	0.321 (0.63)	0.238 (0.67)
$s(H^{\mathrm{E}}_{\mathrm{m}})$	1457.0 (0.47)	1306.5 (0.47)	84.7 (0.97)	65.9 (0.98)		414.1 (0.63)
			Butyl Ethanoate (1) + *tert*-Butyl Alcohol (2)[f]			
$s(Q)$	0.007 (0.91)	0.008 (0.89)	0.014 (0.77)	0.004 (0.96)	0.096 (0.54)	0.013 (0.78)
$s(\gamma)$	0.015 (0.97)	0.016 (0.97)	0.039 (0.86)	0.015 (0.98)	0.329 (0.60)	0.073 (0.71)
$s(H^{\mathrm{E}}_{\mathrm{m}})$	1268.3 (0.47)	1219.2 (0.47)	85.4 (0.97)	98.6 (0.96)		277.5 (0.74)
			Butyl Propanoate (1) + *tert*-Butyl Alcohol (2)[f]			
$s(Q)$	0.002 (0.99)	0.003 (0.98)	0.008 (0.90)	0.004 (0.97)	0.101 (0.55)	0.009 (0.88)
$s(\gamma)$	0.015 (0.98)	0.016 (0.97)	0.036 (0.87)	0.016 (0.97)	0.456 (0.57)	0.054 (0.73)
$s(H^{\mathrm{E}}_{\mathrm{m}})$	1253.7 (0.47)	1184.0 (0.47)	97.1 (0.96)	166.4 (0.91)		339.4 (0.66)
			Butyl Butanoate (1) + *tert*-Butyl Alcohol (2)[f]			
$s(Q)$	0.003 (0.99)	0.003 (0.98)	0.009 (0.92)	0.005 (0.94)	0.102 (0.57)	0.011 (0.87)
$s(\gamma)$	0.037 (0.90)	0.039 (0.88)	0.062 (0.74)	0.020 (0.97)	0.472 (0.57)	0.123 (0.71)
$s(H^{\mathrm{E}}_{\mathrm{m}})$	1354.6 (0.47)	1242.8 (0.47)	108.3(0.95)	248.8 (0.82)		319.0 (0.68)

[a] $Q = G^{\mathrm{E}}_{\mathrm{m}}/RT$. $s(\gamma)$ is the global standard deviation for two activity coefficients. Between parentheses is the corresponding goodness of fit, r^2. [b] Ref 4. [c] Ref 5. [d] Ref 2. [e] Ref 1. [f] Ref 3.

Gibbs function do not give an independent statistical information. With these hypotheses, the objective function used was

$$\mathrm{OF} = \sum_{i=1}^{q}\left[\frac{H^{\mathrm{E}}_{\mathrm{m}}/RT(T_i, x_{1i}) - (H^{\mathrm{E}}_{\mathrm{m}}/RT)_i}{(H^{\mathrm{E}}_{\mathrm{m}}/RT)_i}\right]^2 + \sum_{i=1}^{2}\sum_{j=1}^{n}\left[\frac{\ln \gamma_i(T_j, x_{ij}) - \ln \gamma_{ij}}{\ln \gamma_{ij}}\right]^2 \qquad (10)$$

where $\gamma_i(T_j, x_{ij})$ are the activity coefficients calculated by the model for the Gibbs function (eq 8) while γ_{ij} are experimental values at the same concentration and temperature (Table 7). Analogously, values for the enthalpies of $H^{\mathrm{E}}_{\mathrm{m}}(T_i, x_{1i})/RT$ and $(H^{\mathrm{E}}_{\mathrm{m}}/RT)_i$ correspond, respectively, with the theoretical and experimental ones. Owing to the complexity of the problem of optimizing eq 10 with classical methods based on the gradient of the function to be optimized and, especially, the need to achieve global optimum values, correlation of data with minimization of OF was carried out using a genetic algorithm.[21] The procedure for this has been described in previous papers.[1,22]

Table 7 shows the results obtained with the model proposed for the four mixtures of propyl esters (1) + *tert*-butyl alcohol (2). It can be observed that the values obtained for the statistical parameters are quantitatively acceptable, and the qualitative evaluation of the representations, shown in Figure 5 (solid lines), is also good. To check the goodness of fit of these correlations, estimations made with the classical models UNIQUAC, Wilson, and NRTL, using the same regression procedure and the same objective function defined in ref 10, are recorded in the first three columns of Table 8. For the latter model, the parameter α has been left free in the regression procedure since, if instead of this the recommended value for this type of mixtures is fixed at $\alpha = 0.3$, the correlations obtained are unacceptable. Quantitative evaluations of all the models are recorded in the same table with the goodness of fit, s and r^2, for each case. In summary, the model proposed in this work, considering the data for (propyl esters + *tert*-butyl alcohol), is the most appropriate to use to represent isobaric VLE data and excess enthalpies, but only the NRTL model approaches this qualification when the value of the α parameter is optimized in the regression procedure. The UNIQUAC and Wilson models offer acceptable activity coefficients although values predicted for enthalpies of the mixtures are rather deficient. To verify once again the utility of the model proposed, we present a summary of the evaluation in Table 9, which is similar to that recorded in Table 8 for propyls, and with the same four correlations applied to the mixtures of the other alkyl (methyl to butyl) alkanoates with the same tertiary alkanol, making a total of 12 binary systems. A detailed analysis of Table 9 clearly supports carrying out the correlation with the model proposed in this work; see eq 8, which was used in its simplest form for the set of ethyl esters[1] or in its broadest form with a greater number of coefficients for methyls[2] and butyls.[3] As shown in Table 9, the estimations of equilibrium quantities and the enthalpies were equally acceptable, showing significantly better results in all cases than those obtained with the Wilson, UNIQUAC, and NRTL models. The only exception observed was for mixtures of (butyl esters + *tert*-butyl alcohol), for which the NRTL model estimated values of H_m^E were closer to experimental values, although estimations of γ_i and G_m^E were better with the model proposed here.

Prediction of VLE Data. For this work, the prediction of isobaric VLE data was done using two versions of the UNIFAC group contribution model, the original one with the most recent version incorporating parameters proposed by Hansen et al.[4] and Gmehling et al.[5] This latter has a higher prediction capacity and can predict VLE data at 101.32 kPa and mixing enthalpies using the same set of interaction parameters. For the four mixtures in this work, application of the method using both versions gave the results recorded graphically in Figure 5a−d together with experimental values. It is clear that the estimations made by both versions are almost identical for the mixtures of (propyl methanoate + *tert*-butyl alcohol), possibly because in both cases the same systems were used to obtain the interactions CH_2/HCOO and OH/HCOO. However, the results are very different from those obtained for the remaining systems. The general tendency is that for the UNIFAC version, with the parameters of Hansen et al.,[4] to give estimations of VLE data far higher than real values. The version of Gmehling et al.,[5] however, produces values below real values. The quantitative evaluation is recorded in Table 8, with a goodness of fit to experimental data that did not reach $r^2 = 0.80$ in any case.

To summarize, Table 9 records the quantitative evaluation of the UNIFAC application of the other 12 mixtures with *tert*-butyl alcohol done for this research project. The global evaluation is that there is no clear rule that a specific method gives better estimations than any other, although the differences obtained with the version of Gmehling et al.[5] are smaller. Figure 4a−d shows the estimations of vapor concentration and equilibrium temperatures represented, respectively, as $(y - x)$ versus x and T versus x, for each of the propyl ester systems. For the (propyl methanoate + *tert*-butyl alcohol) mixture, none of the procedures gives a good estimation, although for the remaining mixtures, the UNIFAC method, with parameters of Gmehling et al.,[5] is acceptable both for y and for T, which is also quantitatively verified in Table 8 for other equilibrium quantities. The method that uses the parameters of Hansen et al.[4] establishes an azeotrope for the (propyl ethanoate + *tert*-butyl alcohol) mixture, which is not confirmed by experimentation. Finally, with regards to the mixtures with propyl esters it is noteworthy that, in the estimation of enthalpies using the version of Gmehling et al.,[5] yield values of H_m^E are always lower than real values, and these differences increase with the acid chain length of the propyl ester. However, the predictions of H_m^E with temperature are of the same sign as experimental values (i.e., with a coefficient $(\partial H_m^E/\partial T)_p < 0$).

Finally, it is noteworthy that application of the UNIFAC method in the two versions mentioned here to the whole group of 16 binary mixtures {alkyl (methyl to butyl) alkanaotes (methanoate to butanoate) + *tert*-butyl alcohol} is recorded together with its results in Table 9. The clearest conclusion that can be drawn from evaluating all the systems together, including the propyl ones in Table 8, is that the UNIFAC model, with the parameters of Hansen et al.,[4] is not suitable with the current values of the interaction parameters to estimate the properties of the isobaric liquid−vapor equilibrium for (ester + *tert*-butyl alcohol) systems. If the same model is used, but applying the version proposed by Gmehling et al.,[5] the estimations are better except for a few cases. The most significant differences are observed for the mixtures of alkyl methanoates, clearly indicating that the interaction with the HCOO- group both in the CH_2/HCOO and in the OH/HCOO require new values. These will be investigated in the following project since the systems that contain these (methanoates + alkanes) have not yet been studied in depth. Estimation of the enthalpies with this same model gives results that differ from experimental values by about 20 %, with the greatest differences being obtained, as with VLE data, in the alkyl methanoate mixtures.

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