444 *J. Chem. Eng. Data* **2005,** *50,* 444−454

Vapor−Liquid Equilibria at 101.32 kPa and Excess Properties of Binary Mixtures of Butyl Esters + *tert*-Butyl Alcohol

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This work shows the experimental values of excess properties H_m^E and V_m^E at two temperatures and the isobaric vapor−liquid equilibria at 101.32 kPa for binary systems composed of the first four butyl alkanoates with *tert*-butyl alcohol. None of the mixtures presented azeotropes, and all of the experimental data $p-T-x-y$ were checked with a point-to-point test, proving to be thermodynamically consistent. The correlation of vapor−liquid equilibria and excess enthalpies was done simultaneously using different expressions with temperature-dependent coefficients. The model that gave the most acceptable correlation for the four mixtures was the polynomial expression proposed in this work. The NRTL model gave acceptable estimations of H_m^E, and the UNIQUAC, of equilibrium data. Two versions of the UNIFAC model were used: the original one with parameters by Hansen et al. and the version modified by Gmehling et al., which predicts the equilibrium data as the mixing enthalpies. This last version estimated H_m^E with differences of around 20% for the four mixtures at different temperatures. The predictions made for equilibria are considered to be acceptable for the mixtures (butyl propanoate or butanoate + *tert*-butanol). The estimations made using the original version by Hansen et al. were not good.

Introduction

This is the third paper in a series of studies on binary mixtures of alkyl alkanoates with *tert*-butyl alcohol. As with the two previous works,[1,2] we present here the excess enthalpies and volumes, H_m^E and V_m^E, and the vapor−liquid equilibria (VLE) measured at constant pressure for a set of four binary mixtures composed of butyl esters (methanoate to butanoate) with the tertiary alkanol of butanol. This series forms part of a wider research project on systems that contain alkanols; this project attempts not only to analyze the results and behavior of associated compounds but also to improve the mathematical treatment of thermodynamic data by using a new equation whose efficacy we try to check and a procedure to estimate its parameters.

Specifically, for this work excess quantities H_m^E and V_m^E have been determined at temperatures of 299.15 K and 318.15 K for the former and at 303.15 K and 318.15 K for the latter, whose analysis will improve the knowledge of this type of system, and the data corresponding to the isobaric VLE at 101.32 kPa. For the properties mentioned, there are no published data in the literature corresponding to the mixtures selected for this work.

Experimental data were treated with a model previously used in other works,[1−3] the efficacy of which could be confirmed here with the simultaneous fit of VLE and H_m^E data. To do this, the results will be compared with those obtained by two classical methods in the treatment of VLE data, NRTL and UNIQUAC. Similarly, to improve the predictive ability of the group contribution UNIFAC method, it is interesting to know its utility for mixtures containing a tertiary alkanol. The original version of the UNIFAC model with parameters of Hansen et al.[4] is simpler and more restricted; however, until now the estimated values were not acceptable for mixtures containing *tert*-butyl alcohol.[1,2] It may be necessary to recalculate the parameters corresponding to ester + alkane and ester + alkanol interactions, which we will do shortly when we have sufficient data for these systems. Another version of the UNIFAC model, proposed by Gmehling et al.,[5] has offered better predictions for this type of system, for both VLE properties and excess enthalpies. Bearing in mind that this latter version presents an exclusive value for the group parameters of volume and area of the tertiary alkanol, having also previously observed a wide versatility in the model with respect to ester, we find that it can be applied to methanoates, ethanoates, or other alkyl alkanoates.

Experimental Section

Materials. Butyl esters and *tert*-butyl alcohol were from Aldrich Co., and in both cases, we used samples with the highest purity manufactured by that manufacturer. Before their experimental use, all products were degassed with ultrasound and treated with a desiccant (molecular sieves, type 0.3 nm, Fluka) for several days in the dark to eliminate any trace of moisture. After these treatments, the quality of the compounds was tested with a GC model HP-6890 equipped with an FID, and the resulting degree of purity coincided with that indicated by the manufacturer for all compounds. Moreover, some physical properties such as the normal boiling point $T_{b,i}^o$, the density ρ, and the refractive index n_D at two temperatures (303.15 K and 318.15 K) were determined experimentally. It is common practice in the field of mixture thermodynamics to present measurements at the standard temperature of 298.15 K, but because *tert*-butyl alcohol has a melting point of 298.81 K that is well known in the literature[6], the temperature 303.15 K was chosen for the densities and 299.15 K was

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10.1021/je0497350 CCC: $30.25

Table 1. Physical Properties of Pure Substances

compound	mass fraction	$T^{\circ}_{\mathrm{b,exptl}}$/K	$T^{\circ}_{\mathrm{b,lit}}$/K	T/K	ρ_{exptl}/$\mathrm{kg \cdot m^{-3}}$	ρ_{lit}/$\mathrm{kg \cdot m^{-3}}$	$n_{\mathrm{D,exptl}}$	$n_{\mathrm{D,lit}}$
tert-butanol	0.997	355.58	355.50[a]	303.15→	775.39	775.45[a]	1.3821	1.3823[c]
				303.15→		775.7[c]		
				318.15→	759.87	759.45[b]	1.3741	
butyl methanoate	0.970	379.33	379.3[a]	303.15→	883.40	881.8[d]	1.3836	
			379.25[b]	318.15→	867.74	866.3[d]	1.3773	
butyl ethanoate	0.997	399.18	399.21[a]	303.15→	871.35	871.29[a]	1.3892	
			399.15[b]	303.15→		871.8[d]		
				318.15→	855.42	856.5[d]	1.3821	
butyl propanoate	0.990	418.07	419.75[b]	303.15→	866.14	866.6[d]	1.3963	
				318.15→	851.33	852.0[d]	1.3891	
butyl butanoate	0.980	438.09	438.15[b]	303.15→	860.17	862.3[d]	1.4018	
				318.15→	846.13	849.3[d]	1.3950	

[a] Riddick et al.[6] [b] Daubert and Danner.[7] [c] Wilhoit et al.[8] [d] Values obtained by interpolation from TRC.[9]

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

x_1	$10^9 V^{\mathrm{E}}_{\mathrm{m}}$/$\mathrm{m^3 \cdot mol^{-1}}$	x_1	$10^9 V^{\mathrm{E}}_{\mathrm{m}}$/$\mathrm{m^3 \cdot mol^{-1}}$	x_1	$10^9 V^{\mathrm{E}}_{\mathrm{m}}$/$\mathrm{m^3 \cdot mol^{-1}}$	x_1	$10^9 V^{\mathrm{E}}_{\mathrm{m}}$/$\mathrm{m^3 \cdot mol^{-1}}$	x_1	$10^9 V^{\mathrm{E}}_{\mathrm{m}}$/$\mathrm{m^3 \cdot mol^{-1}}$	x_1	$10^9 V^{\mathrm{E}}_{\mathrm{m}}$/$\mathrm{m^3 \cdot mol^{-1}}$
303.15 K											
Butyl Methanoate (1) + *tert*-Butyl Alcohol (2)											
0.0523	156	0.2492	531	0.4437	670	0.5630	652	0.7058	535	0.8620	299
0.1023	275	0.3113	599	0.4502	671	0.5988	630	0.7430	488	0.9082	211
0.1566	385	0.3577	635	0.5163	669	0.6462	596	0.7961	411	0.9569	104
0.2016	463										
Butyl Ethanoate (1) + *tert*-Butyl Alcohol (2)											
0.0574	176	0.2462	539	0.3993	659	0.5624	641	0.7069	525	0.8654	310
0.0965	271	0.3081	604	0.4482	669	0.6068	614	0.7606	462	0.8979	248
0.1524	396	0.3513	632	0.4516	670	0.6521	579	0.8085	398	0.9379	157
0.2027	478	0.3544	636	0.5027	664						
Butyl Propanoate (1) + *tert*-Butyl Alcohol (2)											
0.0560	122	0.2532	420	0.4055	528	0.5567	537	0.6981	458	0.8657	257
0.0989	205	0.3022	464	0.4627	541	0.6006	520	0.7560	403	0.9114	184
0.1515	292	0.3577	505	0.5047	548	0.6479	494	0.8104	349	0.9409	137
0.2004	349										
Butyl Butanoate (1) + *tert*-Butyl Alcohol (2)											
0.0471	98	0.2500	436	0.3939	550	0.5482	570	0.7029	481	0.8412	307
0.0954	197	0.3007	487	0.4803	571	0.6008	551	0.7639	418	0.9007	204
0.1464	282	0.3484	518	0.4891	574	0.6449	529	0.8020	369	0.9256	157
0.1994	365										
318.15 K											
Butyl Methanoate (1) + *tert*-Butyl Alcohol (2)											
0.0703	216	0.2245	549	0.3799	674	0.5323	683	0.7185	553	0.8510	367
0.1320	370	0.2645	590	0.4451	693	0.5839	664	0.7881	461	0.9366	174
0.1841	473	0.3230	657	0.5004	691	0.6526	613				
Butyl Ethanoate (1) + *tert*-Butyl Alcohol (2)											
0.0632	194	0.2082	463	0.3438	631	0.5062	678	0.7359	572	0.8574	373
0.1239	340	0.2556	531	0.4052	659	0.5564	670	0.7617	522	0.9049	262
0.1517	389	0.2946	565	0.4526	671	0.6192	655				
Butyl Propanoate (1) + *tert*-Butyl Alcohol (2)											
0.0631	135	0.1956	351	0.3215	481	0.4620	555	0.6541	534	0.8379	332
0.0813	168	0.2204	381	0.3663	519	0.5319	571	0.7503	453	0.9199	185
0.1271	250	0.2772	442	0.4254	546	0.5927	561				
Butyl Butanoate (1) + *tert*-Butyl Alcohol (2)											
0.0484	150	0.1698	344	0.2848	468	0.4547	557	0.6522	537	0.8126	372
0.0835	215	0.2146	399	0.3429	506	0.5137	575	0.6925	507	0.8937	245
0.1234	284	0.2273	409	0.3839	538	0.5666	568				

chosen for the enthalpies. Table 1 shows the values obtained for the physical properties of the substances used and their comparison with those reported in the literature, showing good agreement with direct experimental values when certain differences in the densities exist because these values were obtained by interpolation.

Apparatus and Procedure. The excess enthalpies $H^{\mathrm{E}}_{\mathrm{m}}$ of the binary mixtures of butyl esters + *tert*-butyl alcohol were determined isothermically at temperatures of 299.15 K and 318.15 K. The uncertainty in the temperature of the Calvet microcalorimeter used (model MS80D, Setaram) was around ±0.01 K, and the equipment was calibrated electrically and regularly at the two working temperatures with a Joule effect. The uncertainty in the experimental results was estimated to be lower than 1% for $H^{\mathrm{E}}_{\mathrm{m}}$ and around $\pm 2 \times 10^{-4}$ for the mole fractions of each of the butyl esters. The resolution of the system was verified by comparing the values obtained for the ethanol + nonane

Table 3. Excess Molar Enthalpies, H^E_m, for Binary Systems of Butyl Esters (1) + *tert*-Butanol (2) at Two Different Temperatures

x_1	H^E_m/J·mol^{-1}	x_1	H^E_m/J·mol^{-1}	x_1	H^E_m/J·mol^{-1}	x_1	H^E_m/J·mol^{-1}	x_1	H^E_m/J·mol^{-1}	x_1	H^E_m/J·mol^{-1}
299.15 K											
Butyl Methanoate (1) + *tert*-Butyl Alcohol (2)											
0.0488	428.6	0.2215	1445.9	0.3871	1904.9	0.5184	1963.6	0.6382	1803.1	0.8536	979.5
0.1038	809.6	0.2795	1657.5	0.4356	1953.9	0.5201	1959.1	0.7060	1622.7	0.9292	532.4
0.1626	1165.1	0.3344	1807.2	0.4803	1969.1	0.5762	1919.5	0.7783	1346.6		
Butyl Ethanoate (1) + *tert*-Butyl Alcohol (2)											
0.0489	314.5	0.2101	1158.7	0.3620	1642.4	0.5053	1833.8	0.6844	1598.4	0.8423	1005.5
0.0993	611.8	0.2646	1364.6	0.4090	1733.6	0.5507	1822.7	0.7606	1356.7	0.9195	583.3
0.1534	900.9	0.3182	1524.9	0.4531	1796.2	0.6122	1751.2				
Butyl Propanoate (1) + *tert*-Butyl Alcohol (2)											
0.0382	226.9	0.1782	947.2	0.3251	1446.9	0.4387	1673.1	0.5753	1710.7	0.8170	1104.7
0.0828	473.2	0.2280	1139.8	0.3706	1555.8	0.4545	1703.2	0.6485	1618.7	0.9058	665.9
0.1301	723.1	0.2773	1305.4	0.4145	1639.5	0.5113	1729.1	0.7288	1434.6		
Butyl Butanoate (1) + *tert*-Butyl Alcohol (2)											
0.0368	208.7	0.1658	865.2	0.3063	1374.0	0.4169	1623.4	0.6147	1641.2	0.7960	1159.9
0.0754	411.3	0.2126	1053.2	0.3463	1479.3	0.4735	1685.2	0.6989	1482.2	0.8990	664.4
0.1200	662.9	0.2602	1223.7	0.3862	1556.5	0.5383	1698.0				
318.15 K											
Butyl Methanoate (1) + *tert*-Butyl Alcohol (2)											
0.0456	358.9	0.2122	1287.2	0.3780	1775.0	0.4852	1920.4	0.6515	1796.8	0.8641	954.6
0.0976	705.3	0.2697	1501.0	0.4267	1855.2	0.5340	1923.6	0.7188	1608.3	0.9367	507.8
0.1519	1011.3	0.3251	1663.5	0.4384	1874.7	0.5898	1896.1	0.7904	1332.3		
Butyl Ethanoate (1) + *tert*-Butyl Alcohol (2)											
0.0403	306.4	0.1926	1081.7	0.3414	1567.7	0.4550	1767.2	0.6058	1767.9	0.8369	1037.3
0.0856	548.5	0.2461	1288.6	0.3865	1663.8	0.4920	1814.2	0.6796	1628.4	0.9197	577.9
0.1381	828.3	0.2937	1438.0	0.4190	1733.9	0.5485	1808.8	0.7538	1397.5		
Butyl propanoate (1) + *tert*-Butyl Alcohol (2)											
0.0534	358.7	0.2564	1239.6	0.4023	1614.8	0.5104	1707.0	0.6507	1580.0	0.8261	1026.3
0.1182	690.2	0.3166	1435.4	0.4520	1676.9	0.5782	1678.5	0.7363	1368.5	0.8191	551.9
0.1891	995.4	0.3719	1556.6								
Butyl Butanoate (1) + *tert*-Butyl Alcohol (2)											
0.0288	185.0	0.1662	890.1	0.3381	1456.9	0.4728	1667.9	0.5837	1666.3	0.7492	1332.5
0.0688	422.2	0.2221	1114.6	0.3911	1577.5	0.5051	1685.4	0.6336	1612.9	0.8181	1062.5
0.1135	629.0	0.2818	1306.9	0.4266	1626.9	0.5405	1682.6	0.6898	1505.5	0.9049	622.7

mixture at 318.15 K, resulting in H^E_m values close to those reported in the literature[10] with differences smaller than the uncertainties previously indicated for the apparatus.

To determine isobaric VLE, a small glass vessel of around 60 cm^3 was used, operating continuously with recirculation in both phases. The intensive VLE variables p and T are obtained as follows. Control of the pressure, maintained constant at 101.32 kPa, was done with regulator/calibrator equipment manufactured by Desgranges et Huot (model PPC2), which presents an uncertainty of ±0.02 kPa. The temperature at each step of the equilibrium was measured with an ASL-F25 thermometer, calibrated regularly according to ITS-90, which presents an uncertainty in the measurement of ±10 mK.

However, when equilibria were reached with constant values p and T, concentrations of the liquid x_1 and vapor y_1 phases of the binary systems of butyl esters (1) + *tert*-butyl alcohol (2) were determined. To do this, for a specific mixture, the densities of samples obtained from both phases were measured, and the concentrations were calculated using a standard curve of densities versus concentration, calculated previously with samples of known composition at temperatures of 303.15 K and 318.15 K for the four systems. An Anton Paar digital densimeter (model DMA-55) with an uncertainty of ±0.02 kg·m^{-3} was used. The correlations $\rho = \rho(x_1)$ for each mixture were calculated using a simple equation that contains a weighted factor on a second-degree polynomial form of the type $\rho = \sum_{i=1} x_i\rho_i + x_i x_j \sum_{i=0} a_i x_1^i$. The pairs of experimental values (x_1, ρ) 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 to obtain concentrations of mixtures in equilibrium, from the densities of the condensed vapor and liquid phases, was carried out with an uncertainty better than ±0.002 units of the ester mole fraction. For the pairs (x_1, V^E_m), the uncertainty in the calculations of the mole fraction of the ester is $\pm 5 \times 10^{-5}$, and it is $\pm 2 \times 10^{-9}$ m^3·mol^{-1} for V^E_m.

Results

Excess Properties. Table 2 shows the experimental data corresponding to the points (x_1, V^E_m) of the binary mixtures butyl esters (1) + *tert*-butyl alcohol (2), determined at temperatures of 303.15 K and 318.15 K, whereas Table 3 shows the experimental values of the enthalpies (x_1, H^E_m) for the same mixtures, measured at temperatures of 299.15 K and 318.15 K. The selection of the first temperature for H^E_m is justified by avoiding the solidification of *tert*-butyl alcohol, $T^o_{m,i} = 298.81$ K.[6]

The values obtained experimentally for excess properties, represented generically by Y^E_m, have been correlated as a function of ester concentration by the following function:

$$Y^E_m = z_1 z_2 \sum_{i=0}^{2} b_i z_1^i = z_1(1 - z_1)(b_0 + b_1 z_1 + b_2 z_1^2) \text{ where } z_1 = \frac{x_1}{x_1 + k x_2} \quad (1)$$

Table 4. Coefficients and Standard Deviation, *s*, Obtained Using Equation 1 to Correlate the 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) +					
+ butyl methanoate (1)	0.825	2566	45	371	2
+ butyl ethanoate (1)	0.716	2540	−541	1486	7
+ butyl propanoate (1)	0.635	1625	48	1717	6
+ butyl butanoate (1)	0.569	1401	382	2113	5
$T = 318.15$ K					
tert-butanol (2) +					
+ butyl methanoate (1)	0.829	3099	−1644	2005	8
+ butyl ethanoate (1)	0.718	2629	−1728	3471	8
+ butyl propanoate (1)	0.638	1611	−237	2499	4
+ butyl butanoate (1)	0.572	2072	−2241	4513	5

$Y_m^E = H_m^E$ 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) +					
+ butyl methanoate (1)	0.829	7670.6	−1262.1	3259.4	5.6
+ butyl ethanoate (1)	0.727	4964.0	2677.1	2843.9	9.3
+ butyl propanoate (1)	0.648	4315.3	1171.4	6028.9	12.0
+ butyl butanoate (1)	0.584	3806.6	998.6	7239.4	12.1
$T = 318.15$ K					
tert-butanol (2) +					
+ butyl methanoate (1)	0.832	6884.8	−665.6	4074.1	9.9
+ butyl ethanoate (1)	0.728	5291.5	993.9	4546.4	11.6
+ butyl propanoate (1)	0.651	4608.6	602.7	5871.8	9.6
+ butyl butanoate (1)	0.587	4205.9	−245.1	8090.9	10.9

For the specific case of excess volume, the parameter k, which we label k_v, is calculated from $k_v = V_2^o/V_1^o$, where V_i^o corresponds to the molar volume of the pure components of the mixture measured at the same working temperature; see Ortega et al.[11] As shown in previous works,[11,12] similar results are obtained when k_v is calculated from the quotient of the volume parameters $r_i = \sum_k v_k^{(i)} R_k$, where $v_k^{(i)}$ is the whole number that corresponds to the group number of type k in a molecule of component i and R_k corresponds to the group volume values given by van der Waals; see Bondi.[13] However, there are some disadvantages of using this method for the treatment of enthalpies, especially when this concerns one of the compounds selected here, *tert*-butyl alcohol, because this empirical method does not reveal possible structural changes in the compounds such as regioisomeres or changes in temperature; therefore, it is preferable to use real V_i^o data for pure compounds. Correlation of the enthalpy data in Table 3 was also done with eq 1, proposing a fixed value for parameter k, called k_h for enthalpies, and calculated using the expression

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

that produces a weighted value of the quotient of real volumes of the substances with factors that contain the theoretical parameters of area q_i and volume r_i, as shown by Ortega et al.[11,12] The values of q_i are obtained from $q_i = \sum_k v_k^{(i)} Q_k$, and the values of Q_k are from Bondi.[13]

Values of k_v and k_h are shown in the first column of Table 4 for the set of four binary systems studied here. This Table also displays the estimates obtained for coefficients b_i of eq 1, obtained by applying a least-squares procedure, and the standard deviations $s(Y_m^E)$ for each mixture. The experimental results (x_1, V_m^E) and the corresponding calibration curves are shown in Figure 1 for the four systems

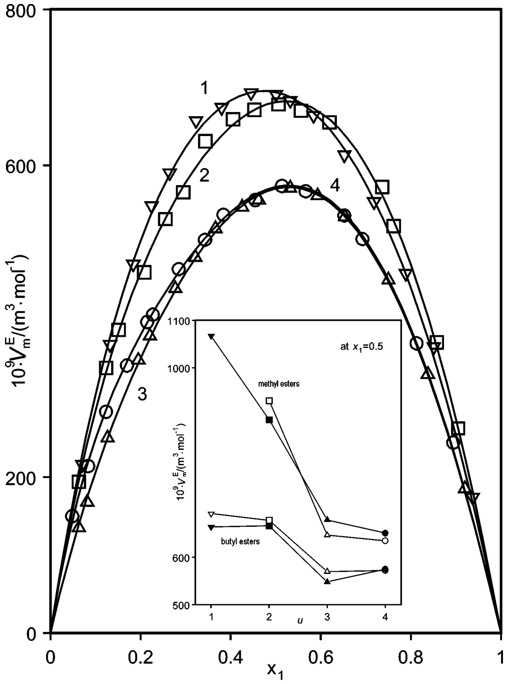

Figure 1. Experimental values and correlation curves of V_m^E vs x_1 at 318.15 K for binary mixtures $C_{u-1}H_{2u-1}COO(CH_2)_3CH_3$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2); labels indicate the u values. The inset shows the variation of equimolar volumes as a function of u and temperature and a comparison between the values for methyl and butyl esters; solid symbols at 303.15 K, open symbols at 318.15 K. ▽, $u = 1$; □, $u = 2$; △, $u = 3$; ○, $u = 4$.

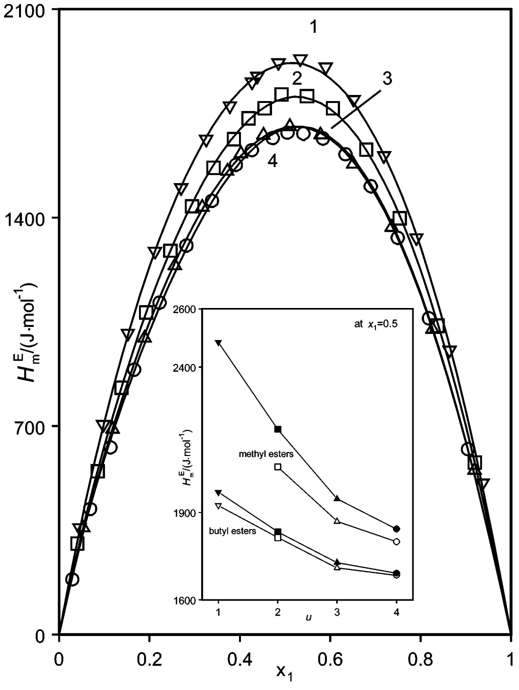

Figure 2. Experimental values and correlation curves of H_m^E vs x_1 at 318.15 K for binary mixtures $C_{u-1}H_{2u-1}COO(CH_2)_3CH_3$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2); labels indicate the u values. The inset shows the variation of equimolar volumes as a function of u and temperature and a comparison between the values for methyl and butyl esters; solid symbols at 299.15 K, open symbols at 318.15 K. ▽, $u = 1$; □, $u = 2$; △, $u = 3$; ○, $u = 4$.

Table 5. Experimental Vapor Pressures, p_i°, for Butyl Alkanoates

T/K	p_i°/kPa	T/K	p_i°/kPa	T/K	p_i°/kPa	T/K	p_i°/kPa	T/K	p_i°/kPa	T/K	p_i°/kPa
Butyl Methanoate											
351.93	39.80	363.94	61.37	372.98	82.86	380.17	104.07	385.84	123.93	390.85	143.71
352.90	41.34	364.53	62.61	373.23	83.42	380.63	105.51	386.31	125.48	391.31	145.47
353.61	42.56	365.28	64.01	374.00	85.54	381.03	106.83	386.58	126.69	391.62	146.81
354.63	44.01	365.82	65.43	374.46	86.83	381.30	107.92	386.93	128.01	391.84	147.92
355.48	45.40	366.39	66.70	374.80	87.98	381.70	109.24	387.32	129.35	392.24	149.45
356.16	46.69	366.97	67.81	375.42	89.51	382.22	110.80	387.69	130.79	392.42	150.41
357.06	48.04	367.70	69.73	375.83	90.70	382.51	112.00	387.92	131.85	392.86	152.16
357.83	49.58	368.21	70.69	376.18	91.92	382.90	113.36	388.37	133.41	393.36	154.53
358.51	50.55	368.77	72.02	376.53	92.98	383.32	114.60	388.60	134.53	393.76	156.14
359.21	52.07	369.20	73.27	377.23	94.84	383.66	116.00	389.06	136.15	393.97	157.28
360.03	53.37	369.77	74.67	377.54	95.98	384.03	117.36	389.38	137.47	394.32	158.68
360.58	54.63	370.39	76.02	377.91	97.12	384.40	118.60	389.73	138.88	394.63	160.14
361.30	56.03	371.01	77.77	378.53	98.83	384.83	120.01	390.04	140.17	394.90	161.36
362.07	57.30	371.35	78.69	378.91	100.02	385.23	121.48	390.26	141.21	395.19	162.84
362.78	58.74	371.83	79.90	379.33	101.32	385.51	122.69	390.58	142.57	395.48	164.08
363.41	60.03	372.32	81.22	379.63	102.50						
Butyl Ethanoate											
369.66	40.29	382.55	61.43	392.35	82.99	400.13	104.16	406.72	125.41	412.24	145.56
370.49	41.48	383.04	62.61	392.55	83.42	401.02	106.99	407.04	126.49	412.59	146.81
371.19	42.64	383.86	64.03	393.89	86.83	401.45	108.04	407.47	128.01	412.90	148.01
372.26	44.02	384.46	65.43	394.26	87.98	401.76	109.22	407.84	129.32	413.19	149.35
373.05	45.37	385.13	66.73	394.68	89.08	402.25	110.79	408.31	130.79	413.61	150.84
373.83	46.58	385.64	67.70	395.39	90.72	402.73	112.04	408.66	132.03	413.93	152.16
374.87	48.12	386.53	69.74	395.76	91.92	403.02	113.10	408.96	133.33	414.27	153.49
375.76	49.58	387.08	70.74	396.37	93.38	403.56	114.64	409.37	134.61	414.48	154.57
376.36	50.55	387.58	72.02	396.86	94.72	403.97	116.02	409.70	136.01	414.80	155.86
377.33	52.07	388.24	73.29	397.26	96.04	404.32	117.33	410.13	137.57	415.25	157.54
378.11	53.38	388.78	74.70	397.70	97.26	404.70	118.57	410.36	138.47	415.49	158.72
378.59	54.37	389.46	76.06	398.30	98.80	405.20	120.05	410.86	140.29	415.75	159.80
379.52	56.01	390.04	77.65	398.75	100.02	405.59	121.55	411.08	141.19	416.19	161.46
380.35	57.30	390.60	78.73	399.18	101.32	405.99	122.71	411.53	142.69	416.51	162.90
381.07	58.69	391.29	80.42	399.56	102.59	406.47	124.36	411.88	144.17	416.74	164.01
381.84	60.07	391.73	81.38								
Butyl Propanoate											
387.18	40.26	400.72	61.25	410.93	82.73	419.08	104.03	425.60	124.01	431.29	143.91
388.03	41.40	401.38	62.70	411.48	83.95	419.61	105.43	426.04	125.41	431.72	145.53
389.10	42.60	402.18	64.23	412.00	85.51	420.08	106.86	426.39	126.63	432.06	146.80
390.14	44.02	402.86	65.35	412.55	86.67	420.46	108.04	426.82	128.04	432.41	148.15
391.06	45.33	403.54	66.67	413.02	87.99	420.89	109.22	427.21	129.35	432.75	149.39
391.78	46.65	404.16	67.83	413.63	89.54	421.38	110.68	427.63	130.85	433.09	150.70
392.85	48.02	404.90	69.61	414.13	90.67	421.80	112.04	427.95	131.99	433.56	152.56
393.76	49.46	405.46	70.61	414.66	91.88	422.28	113.36	428.39	133.39	433.73	153.22
394.42	50.55	406.11	71.99	415.18	93.32	422.69	114.63	428.76	134.72	434.38	155.77
395.28	52.03	406.78	73.29	415.73	94.70	423.12	116.04	429.12	136.00	434.75	157.26
396.18	53.34	407.36	74.67	416.21	96.14	423.56	117.36	429.52	137.44	435.15	158.82
396.91	54.73	408.00	76.11	416.69	97.24	423.97	118.81	429.87	138.73	435.38	159.81
397.72	56.10	408.63	77.38	417.14	98.74	424.39	120.03	430.23	140.03	435.80	161.50
398.53	57.26	409.19	78.73	417.68	100.02	424.78	121.33	430.57	141.24	436.10	162.68
399.29	58.69	409.80	80.02	418.07	101.32	425.20	122.73	430.99	142.76	436.43	164.04
400.03	60.10	410.38	81.65	418.58	102.59						
Butyl Butanoate											
405.54	40.28	419.74	61.31	430.48	82.77	439.18	104.00	446.47	125.37	452.55	145.69
406.59	41.53	420.59	62.83	431.04	84.03	439.66	105.50	446.87	126.64	452.88	146.84
407.56	42.86	421.26	64.02	431.70	85.54	440.16	106.67	447.33	128.00	453.25	148.17
408.56	44.16	422.07	65.51	432.27	86.67	440.68	108.31	447.74	129.33	453.58	149.33
409.28	45.06	422.76	66.81	432.82	87.95	441.11	109.48	448.18	130.73	453.95	150.73
410.43	46.65	423.35	67.91	433.42	89.55	441.60	110.68	448.54	132.01	454.34	152.16
411.38	48.06	424.29	69.74	433.90	90.72	442.01	112.07	448.97	133.41	454.65	153.29
412.43	49.58	424.66	70.42	434.46	91.87	442.53	113.34	449.36	134.68	455.02	154.65
413.11	50.53	425.59	72.31	435.06	93.35	442.93	114.71	449.75	135.99	455.37	155.97
414.21	52.27	426.07	73.25	435.61	94.70	443.44	116.00	450.15	137.35	455.71	157.25
414.92	53.34	426.78	74.67	436.09	96.15	443.86	117.43	450.55	138.69	456.09	158.69
415.87	54.86	427.43	76.02	436.56	97.30	444.34	118.65	450.94	140.07	456.42	159.94
416.72	56.21	428.05	77.34	437.11	98.75	444.78	120.03	451.29	141.21	456.79	161.37
417.51	57.51	428.69	78.82	437.66	100.18	445.21	121.28	451.71	142.69	457.13	162.68
418.27	58.78	429.28	79.99	438.09	101.32	445.62	122.76	452.07	143.97	457.47	164.01
418.98	60.01	430.02	81.71	438.67	102.63	446.04	124.03				

studied at a temperature of 318.15 K. To avoid confusion, values at 303.15 K have not been presented on the same graph because the differences found at the two temperatures are minimal, as can be observed in the inset of the Figure, which presents the change in equimolar values of V_m^E with the ester chain length and temperature. From this graph, one can deduce that $(\partial V_m^E/\partial T)_{p,x}$ is positive for mixtures from butyl methanoate to propanoate and slightly negative for butyl butanoate mixtures. To observe the evolution on the same graph, we have compared the corresponding equimolar volumes obtained here with those obtained for methyl ester systems with the same tertiary alkanol.[2]

Analogously, Table 4 shows the values obtained for the parameters of eq 1 applied to enthalpies and their standard deviations $s(H_m^E)$, and Figure 2 presents the experimental values and the correlation curves of enthalpies at 318.15 K for the four mixtures. (The measurements made at

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

compound	A	B	C	ω	ΔT	ref
				expt; lit	K	
tert-butanol	6.60044	1238.69	85.99		330−370	ref 1
	(2.9984)	(2.4439)	(0.170)	0.614; 0.616[7]		this work
butyl methanoate	6.49980	1488.43	48.10		345−400	this work
	6.52770	1533.40	40.15			ref 6
	6.70820	1627.85	33.17		360−395	ref 13
	(2.9533)	(2.6613)	(0.086)	0.382; 0.384[7]		this work
butyl ethanoate	6.60293	1697.48	29.92		365−420	this work
	6.15144	1368.05	69.22			ref 6
	6.44352	1584.05	42.20		380−415	ref 13
	(3.1066)	(2.9353)	(0.051)	0.417; 0.417[7]		this work
butyl propanoate	6.72425	1860.26	23.89		382−425	this work
	6.57595	1745.90	36.04		400−430	ref 13
	(3.2766)	(3.1309)	(0.040)	0.469; 0.475[7]		this work
butyl butanoate	6.68312	1931.97	25.10		400−460	this work
	6.13153	1500.71	74.43		420−450	ref 13
	(3.2778)	(3.1358)	(0.041)	0.479; 0.485[7]		this work

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

Table 7. Experimental Data, T−x_1−y_1, and Calculated Quantities for the VLE of the Binary Mixtures of Butyl Alkanoate (1) + *tert*-Butanol (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	T/K	x_1	y_1	γ_1	γ_2	G^E_m/RT
Butyl Methanoate (1) + *tert*-Butyl Alcohol (2)																	
355.94	0.0546	0.0385	1.512	1.004	0.026	360.65	0.4824	0.3038	1.142	1.118	0.122	368.18	0.7843	0.5776	1.039	1.253	0.079
356.11	0.0801	0.0556	1.479	1.007	0.037	360.79	0.4899	0.3092	1.139	1.120	0.122	368.74	0.7985	0.5957	1.034	1.260	0.073
356.34	0.1077	0.0733	1.438	1.010	0.048	361.79	0.5473	0.3492	1.113	1.147	0.121	369.16	0.8093	0.6122	1.034	1.259	0.071
356.80	0.1624	0.1072	1.372	1.019	0.067	361.88	0.5497	0.3522	1.114	1.144	0.120	369.92	0.8293	0.6391	1.028	1.277	0.065
357.52	0.2317	0.1507	1.317	1.029	0.086	362.89	0.6010	0.3903	1.091	1.173	0.116	371.02	0.8557	0.6800	1.024	1.291	0.057
357.98	0.2816	0.1797	1.271	1.045	0.099	363.12	0.6089	0.3959	1.084	1.176	0.113	371.93	0.8748	0.7124	1.020	1.298	0.050
358.30	0.3107	0.1967	1.246	1.054	0.105	363.91	0.6454	0.4276	1.076	1.196	0.110	373.25	0.9009	0.7598	1.013	1.312	0.039
358.72	0.3475	0.2189	1.222	1.066	0.112	365.00	0.6856	0.4665	1.065	1.210	0.103	374.45	0.9231	0.8047	1.009	1.323	0.030
358.97	0.3676	0.2310	1.208	1.074	0.114	365.87	0.7168	0.4971	1.055	1.229	0.097	375.76	0.9462	0.8560	1.006	1.337	0.022
359.02	0.3712	0.2333	1.206	1.075	0.115	366.66	0.7408	0.5230	1.047	1.240	0.090	377.16	0.9683	0.9109	1.003	1.344	0.012
359.77	0.4262	0.2682	1.177	1.094	0.121	367.11	0.7535	0.5382	1.043	1.243	0.086	378.21	0.9839	0.9532	1.001	1.345	0.006
359.81	0.4306	0.2695	1.169	1.099	0.121												
Butyl Ethanoate (1) + *tert*-Butyl Alcohol (2)																	
356.06	0.0273	0.0094	1.335	1.000	0.008	365.41	0.4602	0.1735	1.052	1.075	0.062	379.12	0.7898	0.4383	0.993	1.196	0.032
356.60	0.0564	0.0193	1.301	1.001	0.015	366.36	0.4921	0.1904	1.046	1.083	0.062	379.80	0.8004	0.4531	0.992	1.201	0.030
357.21	0.0903	0.0308	1.268	1.003	0.024	367.88	0.5402	0.2168	1.031	1.099	0.060	381.18	0.8211	0.4854	0.993	1.209	0.028
357.78	0.1209	0.0411	1.238	1.005	0.030	368.98	0.5728	0.2361	1.021	1.111	0.057	382.42	0.8382	0.5151	0.994	1.213	0.026
358.40	0.1541	0.0525	1.214	1.009	0.038	370.02	0.6011	0.2548	1.014	1.121	0.054	383.17	0.8487	0.5331	0.993	1.221	0.024
359.17	0.1921	0.0659	1.189	1.013	0.044	370.60	0.6168	0.2653	1.010	1.129	0.052	385.19	0.8737	0.5835	0.994	1.228	0.021
359.75	0.2215	0.0761	1.167	1.018	0.048	371.44	0.6375	0.2815	1.008	1.135	0.051	386.64	0.8906	0.6219	0.995	1.234	0.019
360.77	0.2691	0.0935	1.138	1.025	0.053	372.66	0.6661	0.3045	1.003	1.146	0.048	388.71	0.9125	0.6771	0.996	1.241	0.015
361.53	0.3061	0.1072	1.117	1.035	0.058	373.84	0.6922	0.3281	1.002	1.155	0.046	391.48	0.9395	0.7558	0.996	1.254	0.010
362.37	0.3421	0.1212	1.098	1.043	0.060	374.26	0.7008	0.3361	1.000	1.159	0.044	393.40	0.9565	0.8129	0.997	1.267	0.007
363.29	0.3811	0.1371	1.080	1.054	0.062	375.77	0.7311	0.3669	0.997	1.171	0.040	396.14	0.9782	0.8986	0.998	1.271	0.003
364.18	0.4146	0.1521	1.068	1.061	0.062	377.53	0.7633	0.4038	0.995	1.185	0.036						
Butyl Propanoate (1) + *tert*-Butyl Alcohol (2)																	
355.93	0.0164	0.0030	1.311	1.000	0.005	369.38	0.5016	0.1197	1.046	1.082	0.062	389.93	0.8313	0.3735	1.001	1.203	0.032
356.36	0.0357	0.0065	1.284	1.001	0.010	370.72	0.5351	0.1326	1.036	1.093	0.060	392.65	0.8555	0.4178	1.001	1.208	0.028
356.83	0.0561	0.0102	1.259	1.001	0.014	373.10	0.5921	0.1568	1.020	1.120	0.058	395.03	0.8751	0.4595	1.002	1.215	0.026
357.82	0.0998	0.0182	1.216	1.004	0.023	375.40	0.6348	0.1818	1.020	1.127	0.056	397.51	0.8936	0.5057	1.003	1.219	0.024
358.78	0.1395	0.0258	1.190	1.006	0.029	375.67	0.6421	0.1845	1.014	1.136	0.055	400.72	0.9151	0.5696	1.004	1.222	0.021
359.72	0.1794	0.0335	1.160	1.011	0.036	378.19	0.6851	0.2132	1.010	1.150	0.051	403.85	0.9339	0.6369	1.006	1.221	0.019
360.91	0.2252	0.0434	1.145	1.015	0.042	380.67	0.7231	0.2443	1.010	1.163	0.049	407.02	0.9514	0.7096	1.006	1.226	0.016
362.44	0.2831	0.0565	1.121	1.025	0.050	383.18	0.7567	0.2763	1.007	1.175	0.044	409.28	0.9624	0.7633	1.005	1.222	0.012
363.82	0.3374	0.0691	1.094	1.042	0.058	385.79	0.7885	0.3115	1.002	1.189	0.038	412.30	0.9763	0.8396	1.004	1.221	0.008
365.67	0.3991	0.0856	1.072	1.058	0.062	388.26	0.8149	0.3479	1.002	1.197	0.035	414.45	0.9857	0.8982	1.004	1.221	0.007
367.53	0.4493	0.1021	1.063	1.064	0.061												
Butyl Butanoate (1) + *tert*-Butyl Alcohol (2)																	
356.35	0.0279	0.0028	1.314	0.997	0.004	372.15	0.5472	0.0771	1.015	1.139	0.067	405.23	0.8937	0.3653	0.997	1.278	0.023
357.45	0.0724	0.0072	1.247	0.998	0.015	375.01	0.6037	0.0935	1.008	1.165	0.065	408.59	0.9096	0.4104	0.997	1.284	0.019
358.21	0.1071	0.0106	1.204	1.005	0.025	377.19	0.6406	0.1069	1.005	1.180	0.063	411.74	0.9228	0.4559	0.996	1.285	0.016
359.31	0.1541	0.0152	1.149	1.015	0.034	379.98	0.6831	0.1253	1.003	1.201	0.060	415.44	0.9370	0.5138	0.996	1.289	0.012
360.52	0.2062	0.0208	1.122	1.029	0.046	380.95	0.6968	0.1319	1.001	1.209	0.059	418.51	0.9476	0.5658	0.995	1.289	0.009
361.65	0.2609	0.0261	1.065	1.055	0.056	383.40	0.7268	0.1495	1.001	1.220	0.055	421.55	0.9573	0.6213	0.996	1.288	0.007
363.55	0.3165	0.0342	1.070	1.058	0.060	386.73	0.7617	0.1751	1.001	1.229	0.050	424.94	0.9672	0.6873	0.996	1.286	0.004
365.23	0.3708	0.0421	1.055	1.075	0.065	390.76	0.7998	0.2096	1.001	1.248	0.045	428.57	0.9771	0.7644	0.996	1.285	0.002
366.85	0.4185	0.0498	1.041	1.091	0.067	397.51	0.8502	0.2757	1.000	1.267	0.035	432.69	0.9872	0.8576	0.995	1.276	−0.002
369.29	0.4824	0.0619	1.026	1.114	0.068	401.98	0.8771	0.3257	0.998	1.277	0.028	434.99	0.9927	0.9149	0.997	1.277	−0.002

299.15 K have not been shown to avoid confusion.) The inset shows the change in excess equimolar enthalpy with temperature and the ester chain length. In this case, $(\partial H^E_m/\partial T)_{p,x}$ is negative for the set of four systems studied, although the slope of $H^E_m(T)$ is smaller here than in the case of methyl esters.[2]

Vapor Pressures. Vapor pressures directly affect the amounts that characterize VLE. It is therefore normal to

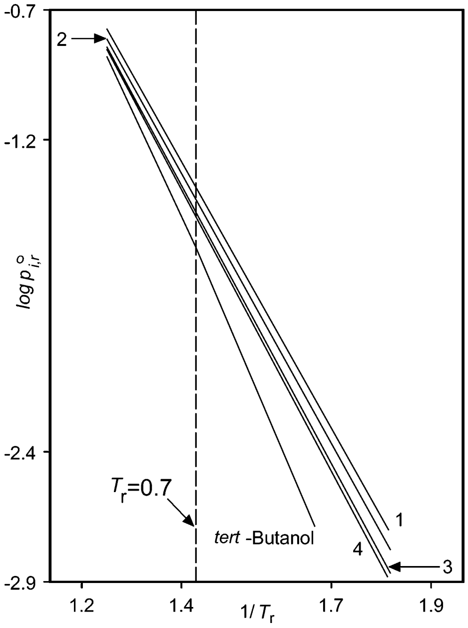

Figure 3. Vapor pressures lines in reduced coordinates for butyl esters $C_{u-1}H_{2u-1}$ $COO(CH_2)_3CH_3$ and *tert*-butanol calculated using the coefficients of Table 6; labels indicate the u values. $T_r = T/T_c$, and $p_r = p/p_c$.

present in our work experimental measurements for the pairs (T, p_i^o) corresponding to the saturation curve of the pure compounds studied and obtained with the same experimental apparatus as the VLE. The vapor pressures of *tert*-butyl alcohol were presented in a previous work,[1] and those corresponding to the butyl esters (methanoate to butanoate) were obtained in our laboratory years ago.[14] It is therefore appropriate to make new measurements using the same equilibration equipment but increasing the temperature range, taking into account at all times the limitations of using a glass ebulliometer. The experimental results of p_i^o versus T for butyl esters are shown in Table 5 and were correlated with the well-known Antoine equation

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

where the constants A, B, and C are determined by a least-squares method; see Table 6, comparing in that Table the values obtained with others reported in the literature that will be used to characterize the VLE of these mixtures. Figure 3 shows the vapor pressure lines of the compounds used in this work (butyl esters and *tert*-butyl alcohol) in reduced coordinates using a similar expression to eq 3 of the form $\log p_{i,r}^o = a - b/(T_r - c)$. Parameters a, b, and c, are obtained by linear regression with the set of values (T_r, $p_{i,r}^o$) minimizing the standard deviation $s(p_{i,r}^o)$. The coefficients obtained are shown in Table 6, but these could have been calculated indirectly from the values A, B, and C, as shown by Ortega et al.[15] However, because the considerations used in that paper are applicable only for a limited range of temperatures, slight differences can be observed between the values of a, b, and c achieved with both methods, which has an effect on on the final values of the acentric factors calculated according to Pitzer's definition,[16] where $\omega = -(\log p_{i,r}^o)_{T_r=0.7} - 1$. It is preferable to calculate these parameters by direct regression and then determine the values of ω, which are recorded in Table 6. These values are in good agreement with those published in the literature and were used for subsequent characterization of the VLE data.

Presentation of VLE Data. The p, T, x_1, and y_1 values obtained directly from the experimentation of isobaric VLE at a pressure of $p = 101.32$ kPa for the four binary mixtures of {(x)butyl esters (methanoate to butanoate) (1) + (1 − x)*tert*-butanol (2)} are compiled in Table 7. On the basis of these, considering the nonideality of the vapor phase, the activity coefficients of the components in the liquid phase are calculated by

$$\ln \gamma_i = \ln\left(\frac{py_i}{p_i^o x_i}\right) + \frac{(B_{ii} - V_i^o)(p - p_i^o)}{RT} + \frac{p}{RT}\sum_j \sum_k y_j y_k (2\delta_{ji} - \delta_{jk}) \tag{4}$$

where $\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$ and where the second virial coefficients B_{ij} for pure compounds and mixtures are calculated from the correlations proposed by Tsonopoulos.[17] 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,[18] using values of the coefficient Z_{RA} reported by Reid et al.[16] The activity coefficients shown in Table 7, obtained with eq 4, are used to obtain values of Gibbs function $G_m^E/RT = \sum x_i \ln \gamma_i$, also shown in Table 7 for each binary system. A version of the point-to-point consistency test proposed by Fredenslund et al.[19] was applied, and in all cases the average difference between the molar fraction of the vapor phase, experimental and calculated by the method, was $\bar{\delta} = \sum_i (y_{i,\text{exptl}} - y_{i,\text{calcd}})/N \le 0.01$ for each equilibrium point, giving a positive validation with the method described.

Figure 4 shows T versus x_1, y_1 and ($y_1 - x_1$) versus x_1 for the four systems of butyl alkanoates (1) + *tert*-butyl alcohol (2). As described in the Introduction, the literature does not publish VLE data for the systems studied here for comparison. None of the mixtures presents an azeotropic point.

Treatment of VLE Data

In this work, the model used is one that was previously presented in former works[1-3] and has a similar form to eq 1 for the simultaneous correlation of experimental isobaric VLE data and excess enthalpies based on the thermodynamic relationship

$$-\frac{H_m^E}{RT} = T\left[\frac{\partial(G_m^E/RT)}{\partial T}\right]_{p,x} \tag{5}$$

and for which the nondimensional energy Gibbs function for a binary mixture takes 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 coefficients b_i, according to eq 5, must be temperature-dependent. If it is also taken into account that the excess thermal capacity is represented through a quadratic relationship with temperature, $C_p^E = \phi(T)$, then a complete expression for the b_i coefficients could be

$$b_i = A_{i1}T^2 + A_{i2}T + A_{i3}\ln T + \frac{A_{i4}}{T} + A_{i5} \tag{7}$$

Now the expression for the excess enthalpy model can be achieved by applying relationship 5 to eq 6 with the

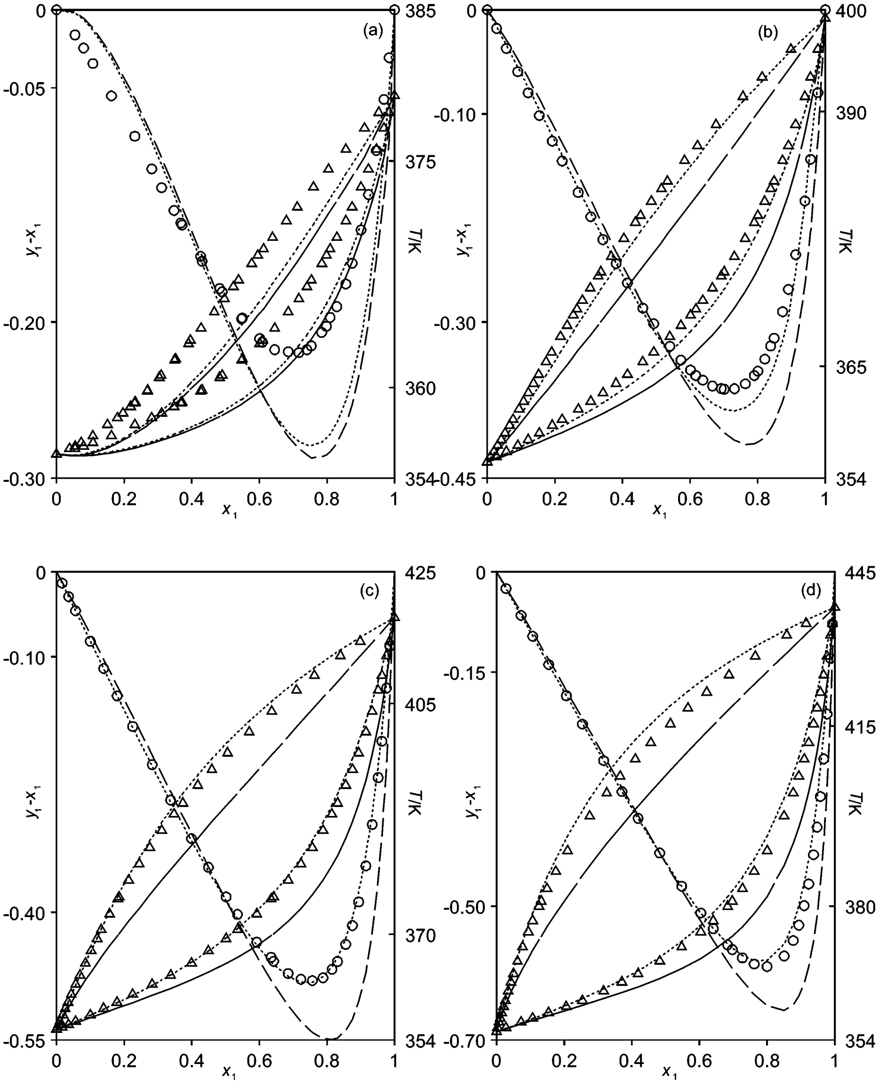

Figure 4. (a−d) Representation of VLE experimental values: ○, ($y_1 - x_1$) vs x_1 and △, T vs x_1, y_1 for binary mixtures $C_{u-1}H_{2u-1}COO(CH_2)_3CH_3$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2). (a) $u = 1$; (b) $u = 2$; (c) $u = 3$; (d) $u = 4$. Dashed lines represent the curves estimated with the UNIFAC model: — —, Hansen et al.;[4] - - -, Gmehling et al.[5]

coefficients of the form in eq 7. This expression finally produces an expression for H^E_m:

$$\frac{H^E_m}{RT}(T, x_1) = z_1 z_2 \sum_{i=0}^{m} \left(\frac{A_{i4}}{T} - 2A_{i1}T^2 - A_{i2}T - A_{i3} \right) z_1^i \quad (8)$$

However, from the practical experience obtained in this and in other works regarding the simultaneous correlation of VLE data and H^E_m, an unnecessary overparametrization can be observed that does not improve the model efficacy. Therefore, in the corresponding analysis, it was more appropriate in eqs 6 and 9 to consider only the terms that corresponded to even powers in z_1. Hence, the simultaneous fit of experimental data comprising the pairs (x_1, H^E_m) and (x_1, G^E_m) was done with a least-squares procedure. The objective function OF that was proposed to be minimized was

$$\mathrm{OF} = \sum_{i=1}^{q} \left[\left(\frac{\dfrac{H^E}{R}(T_i, x_{1i}) - \left(\dfrac{H^E}{R}\right)_i}{\sigma_H} \right) \right]^2 + \sum_{i=1}^{2} \sum_{j=1}^{n} \left[\frac{\ln \gamma_i(T_j, x_{ij}) - \ln \gamma_{ij}}{\sigma_{\gamma i}} \right]^2 \quad (9)$$

where $\gamma_i(T, x_i)$ are the activity coefficients calculated by the model of the Gibbs function (eq 6), whereas γ_i corresponds to experimental values at the same concentration. The denominators σ_H and σ_γ are the standard deviations of the corresponding differences between the experimental values and those of the model for the enthalpies and the activity coefficients, respectively. Equation 9 shows that, as the OF is defined now, this does not take into consideration the values of the Gibbs function because these, calculated from the natural logarithms of the activity coefficients γ_i, would not provide independent statistical information. Owing to the complexity of the expressions used here and to guarantee that optimum global results are obtained, optimization of the OF is done using a genetic algorithm.[20] The procedure for its application in cases of phase equilibria has been described previously.[1,3]

The third column of Table 8 gives the values estimated for the coefficients of the model proposed for the four systems in this work. To validate the application of this model, the UNIQUAC and NRTL models were also used in the correlation of data using the same regression procedure, recording in columns two and three the coefficients of both of these. In this Table, some statistical validation parameters have also been compiled that define the goodness fit, s, and r^2 (in parentheses) for each case.

Table 8. Results Obtained in the Estimation and Prediction of VLE and Excess Enthalpies Using Different Models and the Fitting Parameters[a]

	estimations				predictions	
			eq 6			
	UNIQUAC	NRTL	A_{0j}	A_{2j}	UNIFAC [4]	UNIFAC [5]
Butyl Methanoate + *tert*-Butanol						
	$\Delta u_{12} = -663.42$	$\Delta g_{12} = -17790.12$	8.5×10^{-6}	-2.9×10^{-5}		
	$\Delta u_{21} = 1070.56$	$\Delta g_{12} = 14333.17$	-1.214×10^{-2}	4.548×10^{-2}		
		$\alpha = -0.056$	-4.964×10^{-1}	-4.860×10^{-1}		
			−247.55	3642.67		
			7.15	−19.42		
				$k = 0.519$		
$s(G^E_m/RT)$	0.015(0.83)	0.011(0.92)		0.013(0.98)	0.070(0.62)	0.054(0.67)
$s(\gamma_i)$	0.028(0.96)	0.037(0.94)		0.015(0.99)	0.321(0.63)	0.238(0.67)
$s(H^E_m)$	1457.0(0.47)	84.6(0.97)		65.9(0.98)		414.1(0.63)
Butyl Ethanoate + *tert*-Butanol						
	$\Delta u_{12} = -587.81$	$\Delta g_{12} = 15158.09$	4.2×10^{-5}	9.7×10^{-5}		
	$\Delta u_{21} = 823.39$	$\Delta g_{21} = -18774.34$	-2.553×10^{-2}	-8.727×10^{-2}		
		$\alpha = -0.048$	−2.103	9.326×10^{-2}		
			296.59	−2704.38		
			15.62	25.59		
				$k = 1.178$		
$s(G^E_m/RT)$	0.007(0.91)	0.014(0.77)		0.004(0.96)	0.096(0.54)	0.013(0.67)
$s(\gamma_i)$	0.015(0.97)	0.039(0.86)		0.015(0.98)	0.329(0.60)	0.073(0.71)
$s(H^E_m)$	1268.3(0.47)	85.4(0.97)		98.6(0.96)		277.5(0.74)
Butyl Propanoate + *tert*-Butanol						
	$\Delta u_{12} = 597.93$	$\Delta g_{12} = 11701.37$	-3.9×10^{-6}	-5.1×10^{-6}		
	$\Delta u_{21} = -411.12$	$\Delta g_{21} = -14992.76$	1.389×10^{-2}	2.150×10^{-2}		
		$\alpha = -0.072$	6.845×10^{-1}	7.049×10^{-1}		
			1637.93	3314.30		
			−12.92	−20.05		
				$k = 0.467$		
$s(G^E_m/RT)$	0.002(0.99)	0.008(0.90)		0.004(0.97)	0.101(0.55)	0.009(0.88)
$s(\gamma_i)$	0.015(0.98)	0.036(0.87)		0.016(0.97)	0.456(0.57)	0.054(0.73)
$s(H^E_m)$	1253.7(0.47)	97.14(0.96)		166.4(0.91)		339.4(0.66)
Butyl Butanoate + *tert*-Butanol						
	$\Delta u_{12} = 1231.04$	$\Delta g_{12} = 10628.23$	4.1×10^{-5}	-4.2×10^{-5}		
	$\Delta u_{21} = -877.55$	$\Delta g_{21} = -13667.74$	-1.007×10^{-2}	3.195×10^{-2}		
		$\alpha = -0.09$	3.955×10^{-1}	-6.610×10^{-2}		
			2308.57	830.71		
			−10.12	−8.14		
				$k = 1.008$		
$s(G^E_m/RT)$	0.003(0.99)	0.009(0.92)		0.005(0.94)	0.102(0.57)	0.011(0.87)
$s(\gamma_i)$	0.037(0.90)	0.062(0.74)		0.020(0.97)	0.472(0.57)	0.123(0.71)
$s(H^E_m)$	1354.6(0.47)	108.32(0.95)		248.8(0.82)		318.9(0.68)

[a] The correlation coefficient, r^2, is given in parentheses.

For the NRTL model, it is noteworthy that the parameter α_{12} has been calculated using the same regression procedure because the results obtained with the value of $\alpha_{12} = 0.3$ for this type of mixture[21] generates unacceptable correlations of H^E_m and VLE data. In all cases, the regression procedure gives negative values of α_{12} or ones close to zero. From the global analysis of the results, although the NRTL model offers better partial estimations of enthalpies, the model proposed here substantially improves the simultaneous correlation of thermodynamic quantities. These considerations can be clearly observed in Figures 5 and 6, which show the curves estimated (solid lines) with the model proposed with an acceptable correlation of experimental values. Figure 6 reflects the differences between experimental data for H^E_m and those obtained by the different models used, with the exception of the UNIQUAC model in which the estimations produce very high errors reflected in the r^2 values in Table 8. The differences reflected in Figure 6a−d between the values of the NRTL model and those of eq 8 are similar for the first three systems, although for the butyl butanoate + *tert*-butyl alcohol mixture the NRTL model noticeably improves the estimation of the experimental data at the two temperatures but, in contrast, the estimation of the VLE is not good. In the global evaluation of VLE and H^E_m data, the model proposed here (eqs 6 and 8) presents better global behavior, and its validity is verified once again in this work.

Prediction of VLE Data. In previous works,[1,2] the version proposed by Gmehling et al.[5] for the UNIFAC method was applied to verify the usefulness of the model for estimating isobaric VLE and the H^E_m of mixtures of alkyl esters and *tert*-butanol. It was deduced that this version makes a regular prediction of the properties mentioned although this model offers specific parameters for areas and volumes of the OH− group of a tertiary alkanol. Similarly, in one of the works[2] the original version of UNIFAC[4] was used with worse results, with differences above 100%. The conclusion reached was that both versions of the model require new parameters at least and, logically, new data for the properties. Therefore, here, once again we confirm the usefulness of the model with other mixtures of butyl esters + *tert*-butyl alcohol. Figure 5a−d shows the estimates of both models for the Gibbs function and for the activity coefficients of VLE, and Figure 4a−d shows those corresponding to the equilibrium concentrations and temperatures. Both models present almost identical predictions

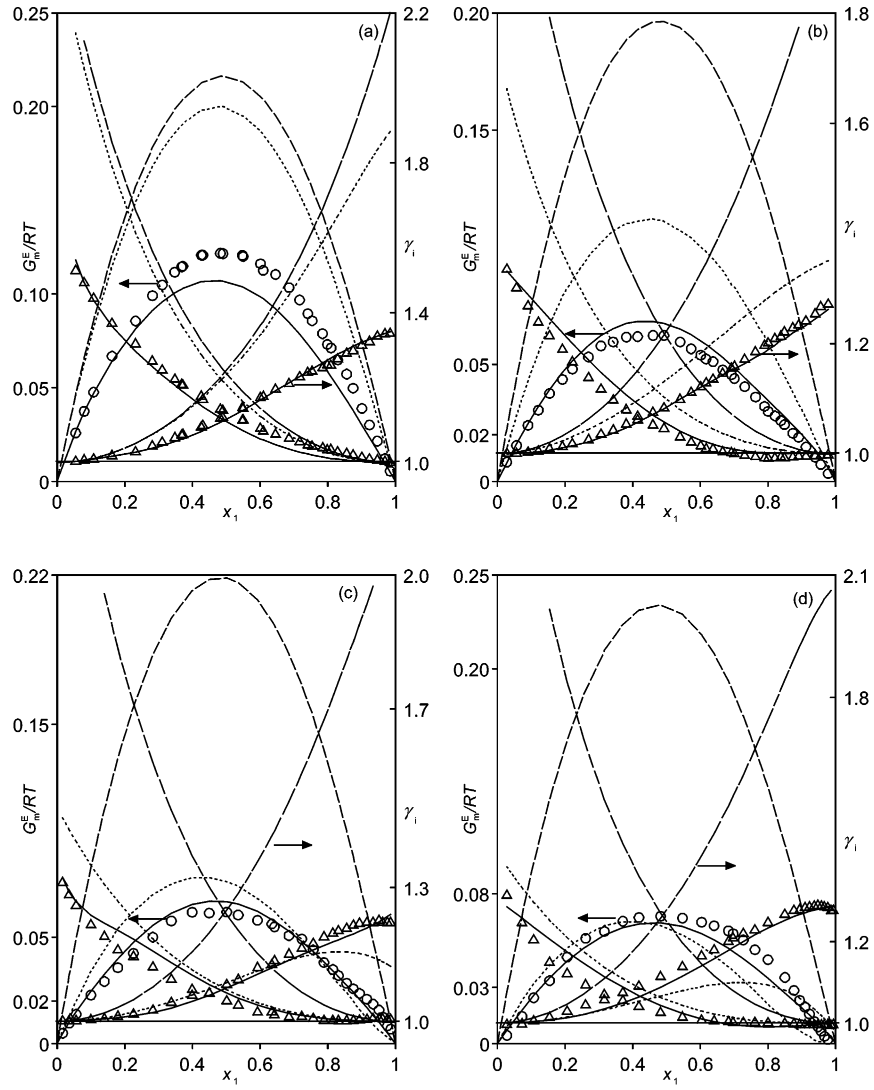

Figure 5. (a−d). Representation of experimental and correlated curves (−) for the quantities G_m^E/RT vs x_1 (○) and γ_i vs x_1 (△) for the binary mixtures $C_{u-1}H_{2u-1}COO(CH_2)_3\ CH_3$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2). (a) $u = 1$; (b) $u = 2$; (c) $u = 3$; (d) $u = 4$. Dashed lines represent the values estimated by the UNIFAC model: − −, Hansen et al.;[4] - - -, Gmehling et al.[5]

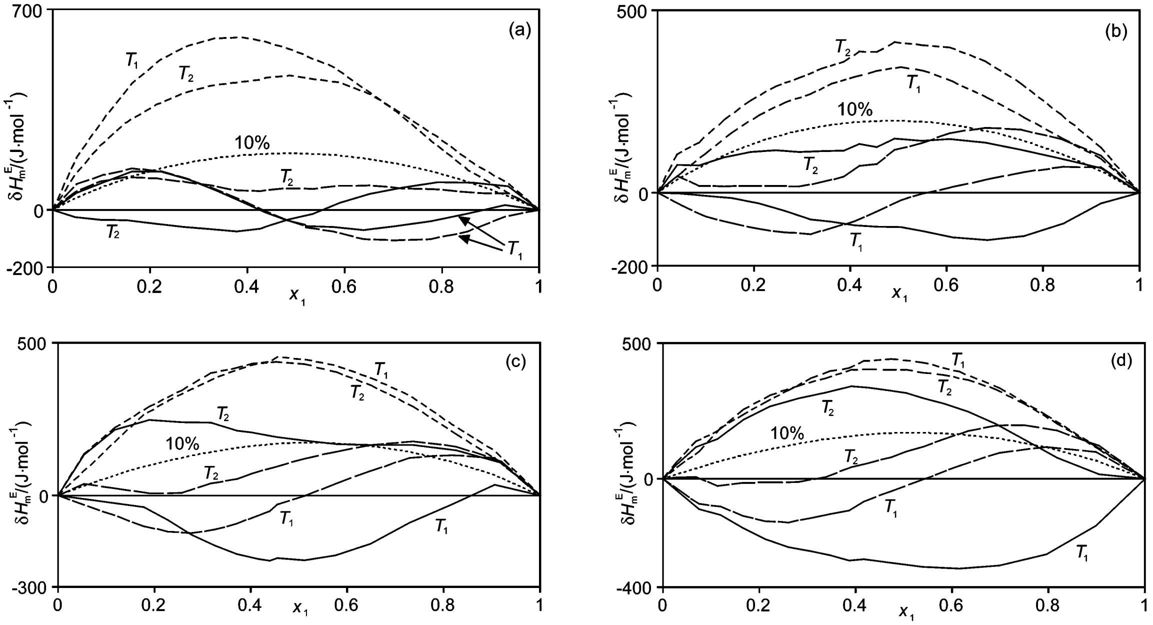

Figure 6. (a−d). Representation of the deviations, $\delta H_m^E = H_{i,\text{calcd}}^E - H_{i,\text{exptl}}^E$, obtained as the differences between the calculated curve by the simultaneous correlation of VLE values, the solid lines by eq 8, the NRTL model (− −), that obtained by UNIFAC5 (- - -) at temperatures of T_1 = 299.15 K and T_2 = 318.15 K, and the corresponding direct experimental values.

for the mixtures composed of butyl methanoate, possibly because they used the same few systems presented in the literature for methanoate/alkane to estimate the specific OH/HCOO interaction. In both cases, predicted VLE values (Figures 4a and 5a) are quite different from experimental values. For the other three mixtures, the version of Hansen et al.[4] produces estimates of G_m^E/RT and of γ_i well above the real values, higher than 200% in all cases. However, the version of Gmehling et al.[5] gives values of G_m^E/RT and of γ_i higher than and very different from experimental values for mixtures of butyl ethanoate + *tert*-butyl alcohol and acceptable values for the other two mixtures (Figure 5c and d) with butyl propanoate and butanoate. For the latter two cases, estimates of concentration and temperature can be considered to be acceptable (Figure 4c and d). This version of the model gives predictions of H_m^E that are lower than the experimental values for the four mixtures studied, with a global average error, at the two temperatures, slightly higher than 20% and very similar to that obtained in a previous work[2] for methyl esters. Similarly, the method produces a variation of $(\partial H_m^E/\partial T)_p > 0$ for the systems containing butyl methanoate, contrary to the experimental value and negative for the other three mixtures, such as occurs in the experimentation.

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Received for review July 20, 2004. Accepted December 20, 2004. This work was financially supported by the Spanish Ministry of Education and Science under project PPQ2004-04404.

JE0497350