Isobaric Vapor−Liquid Equilibria and Excess Quantities for Binary Mixtures of an Ethyl Ester + *tert*-Butanol and a New Approach to VLE Data Processing

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This paper presents the experimental excess properties H_m^E and V_m^E obtained at different temperatures and the vapor−liquid equilibrium values at 101.32 kPa for four binary mixtures composed of four ethyl esters (methanoate to butanoate) and *tert*-butyl alcohol. A point-to-point test applied to the equilibrium values indicated that the systems studied were consistent. The binary mixture ethyl ethanoate + *tert*-butyl alcohol exhibits an azeotropic point at $x_{az} = 0.832$ and $T = 349.59$ K. All values were correlated using a new equation with temperature-dependent coefficients fitting simultaneously the vapor−liquid equilibria and H_m^E values. Good fits were obtained in all cases. Application of a modified version of the UNIFAC model to the mixtures containing a tertiary alkanol yielded rather poor estimates.

Introduction

In the framework of our team's ongoing research program on thermodynamic properties of systems of an alkyl ester + an alkanol and as a part of a systematic study, this paper presents the experimental values and modeling for isobaric vapor−liquid equilibria (VLE) at 101.32 kPa for four binary systems composed of one of the ethyl esters (methanoate to butanoate) and 2-methylpropan-2-ol (*tert*-butyl alcohol). A literature search failed to disclose any VLE values for these binary mixtures except some azeotropic points for the system comprising ethyl ethanoate + *tert*-butyl alcohol.[1] As part of this same study, the molar volumes and excess enthalpies were also determined at two different temperatures. These values were useful for supplementary processing of the VLE values and analyzing the behavior of the mixtures considered. In this connection, Nikam et al.[2] published V_m^E values for the system ethyl ethanoate + *tert*-butyl alcohol at several temperatures, and they will be included for purposes of comparison.

Processing of the experimental values was performed using a new form of an equation employed previously.[3] In an endeavor to assess the efficacy of this new version of the equation, a genetic algorithm[4] was used to fit the VLE and H_m^E values simultaneously. Last, the suitability of the modified-UNIFAC[5] group contribution model in estimating the mixing properties for the mixtures of an ethyl ester with the tertiary alkanol was assessed.

This study, containing the information of a set of experimental values for four binary systems of an ethyl ester + *tert*-butyl alcohol, was intended as a further contribution to other papers dealing with alkyl esters and other isomers of butanol published previously,[6−8] providing new values for addition to the literature and at the same time using those values in a method intended to improve processing of the quantities characterizing the phase equilibria of binary systems.

Experimental Section

Materials. Ethyl esters and *tert*-butyl alcohol employed in the work were of the highest purity commercial grade from Fluka. All them were degassed ultrasonically and dried on a molecular sieve (0.3 nm from Fluka) before use. Component quality was verified by a gas chromatograph (Hewlett-Packard 6890) equipped with a flame ionization detector (FID), and the degree of purity obtained (Table 1) was in all cases consistent with the manufacturer's specifications. The quality was also tested by measuring such physical properties as the normal boiling point $T_{b,i}^0$, the density ρ, and the refractive index n_D, which were used for purposes of comparison. The *tert*-butyl alcohol has a melting temperature[9] of 298.81 K. The measured values for the above-mentioned physical properties have also been summarized in Table 1; on the whole, good agreement with the literature values was observed.

Apparatus and Procedure. The experimental equipment used to determine the isobaric VLE operated dynamically, with refluxing of both phases. System pressure was monitored by a model PPC2 pressure controller/calibrator from Desgranges et Huot, with an uncertainty of ±0.02 kPa. The temperature attained at each equilibrium stage was measured using a model ASL-F25 thermometer, calibrated periodically in accordance with the ITS-90, and had a measurement uncertainty of ±10 mK. The concentrations were calculated from the density curves as obtained using an Anton-Paar (DMA-55) densimeter with an uncertainty of ± 0.02 kg·m^{-3}.

Concentration values for the binary systems consisting of an ethyl ester (1) + *tert*-butyl alcohol (2) at isobaric equilibrium were determined using a standard density versus concentration curve, $\rho = \rho(x_1)$ obtained at temperatures of 303.15 and 318.15 K for each system using samples of known composition, and applying a polynomial equation of second or third degree. The ρ versus x_1 relationships for each mixture were validated by corroborating the quality of the results for V_m^E versus x_1; the uncertainty for the V_m^E was $\pm 2 \times 10^{-9}$ m^3·mol^{-1}. Accord-

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Table 1. Physical Properties of Pure Substances, *tert*-Butanol and Ethyl Esters, Obtained Experimentally

		$T^0_{b,i}$/K		ρ (298.15 K)/kg·m^{-3}		n_D (303.15 K)	
compound	mass fraction	expt	lit	expt	lit	expt	lit
tert-butanol	0.997	355.58	355.57[a] 355.50[b]	775.37[a]	775.7[a]	1.3820	
ethyl methanoate	0.98	327.29	327.46[b,c]	914.53	915.3[b] 914.9[c]	1.3550	
ethyl ethanoate	>0.99	350.25	350.26[b] 350.21[c]	894.44	894.55[b] 894.52[c]	1.3675	1.3675[d]
ethyl propanoate	>0.99	371.91	372.25[b,c]	883.95	884.0[b] 884.42[c]	1.3791	1.3790[d]
ethyl butanoate	>0.98	394.17	394.70[b] 394.65[c]	873.94	873.94[b] 874.11[c]	1.3880	

[a] At 303.15 K, Wilhoit et al. (ref 9). [b] Riddick et al. (ref 10). [c] Daubert and Danner (ref 11). [d] Ortega and Matos (ref 12).

ingly, the back-calculation of the concentrations for the mixtures at equilibrium, after measurement of the densities of the condensed vapor phase and the liquid phase, yielded estimates with a precision better than ±0.002 ester mole fraction units.

The excess enthalpies, H^E_m, were determined isothermically at temperatures of 299.15 and 318.15 K, with an uncertainty of ±0.01 K, using a Calvet model MS80D calorimeter routinely calibrated electrically by a Joule effect. The uncertainties in the experimental results were estimated to be less than 1% of the H^E_m values.

Results and Discussion

Excess Properties. Table 2 shows the excess molar volumes for the ethyl ester + *tert*-butyl alcohol binary systems at known ester concentration determined at 303.15 and 318.15 K. For each binary mixture, the value pairs (x_1, V^E_m) were correlated using a modified version of an equation employed previously,[3] of the form

$$Y^E_m = z_1 z_2 \sum_{i=0}^{m} A_i z_1^{\,i} \qquad (1)$$

where

$$z_i = \frac{x_1}{x_1 + kx_2}$$

with Y^E_m being a generic excess property and where for the volumes, k was set equal to $k_v = V^0_2/V^0_1$, with V^0_i being the molar volume of the pure components of the mixture measured at the working temperature; see Ortega and Alcalde.[13] Table 4 presents the estimated A_i coefficients for eq 1 obtained using a least-squares procedure along with the standard deviation values, $s(V^E_m)$, for each mixture. The results of the correlations have been plotted together with the experimental points for the four systems considered at the working temperature of 303.15 K in Figure 1. The corresponding inset figure depicts the changes in the equimolar V^E_m values with ester chain length and temperature, yielding the positive quantity $(\partial V^E_m/\partial T)_{p,x} > 0$. There was good agreement between our values and those for the system composed of ethyl ethanoate + *tert*-butyl alcohol published by Nikam et al.[2] at $x_1 > 0.5$, but some discrepancies were observed at lower concentrations.

Enthalpies for the four systems were measured at two temperatures, 299.15 K (to avoid the solidification of *tert*-butyl alcohol) and 318.15 K, and the values are presented in Table 3. In this case, the regression of the value pairs (x_1, H^E_m/RT) using the same procedure mentioned above to optimize eq 1 yielded values of k, now designated k_h, by iteration with a view to achieving the best fit. Table 4 lists the coefficients obtained for the correlations and the corresponding standard deviations, $s(H^E_m)$. Figure 2 shows the experimental points and the fitted curves for the enthalpies of the four systems at 299.15 K. The corresponding inset figure depicts the changes in the equimolar excess enthalpies with temperature and ester chain length. The quantity $(\partial H^E_m/\partial T)_{p,x}$ is negative in this case.

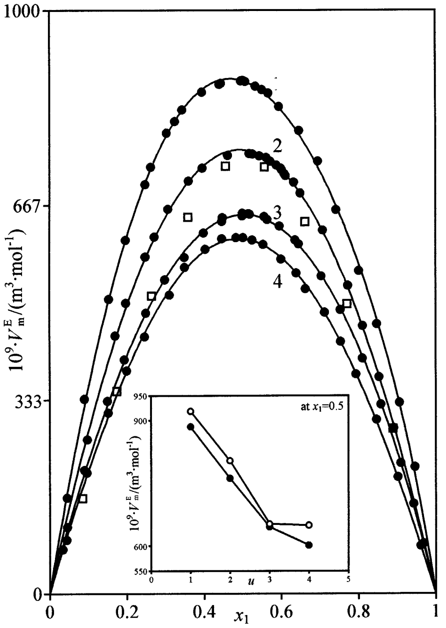

Figure 1. Experimental values (●) and correlation curves for V^E_m vs x_1 at 303.15 K for the binary mixtures $C_{u-1}H_{2u-1}COOC_2H_5$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2); labels indicate the u values. □, Values from Nikam et al. (ref 2); the inset figure shows the changes in equimolar volumes at different values of u and at two temperatures, 303.15 K (●) and 318.15 K (○).

The behavior of mixtures of esters + isobutanol was thoroughly analyzed earlier.[6,14] However, results for other mixtures of a tertiary alkanol and esters are needed for a more in-depth consideration of such systems, including comparisons of the results obtained according to ester chain length and alkanol type.

Vapor Pressures. Vapor pressures influence the values of the VLE quantities, and for that reason our studies ordinarily present experimental measurements for the (T, p^0_i) pairs on the saturation curves for the components employed, obtained using the same experimental equipment used for the VLE values. In this study, the vapor pressures for the four ethyl esters had already been measured at our laboratory.[3,14] Accordingly, vapor pressure

Table 2. Excess Volumes, V^E_m, for Binary Systems of Ethyl Esters (1) + *tert*-Butanol (2) at Two Different Temperatures

x_1	$10^9V^E_m$/m^3·mol^{-1}	x_1	$10^9V^E_m$/m^3·mol^{-1}	x_1	$10^9V^E_m$/m^3·mol^{-1}
T = 303.15 K					
Ethyl Methanoate (1) + *tert*-Butanol (2)					
0.0451	165	0.3957	860	0.5954	835
0.0901	335	0.4411	873	0.6467	794
0.1537	506	0.4445	875	0.6956	742
0.1973	607	0.4964	879	0.7432	659
0.2481	702	0.5013	880	0.8016	554
0.2631	732	0.5084	878	0.8477	463
0.3042	790	0.5344	870	0.9067	328
0.3255	810	0.5515	864	0.9465	217
0.3448	830	0.5677	858		
Ethyl Ethanoate (1) + *tert*-Butanol (2)					
0.0458	114	0.5178	755	0.6336	706
0.0972	265	0.5274	754	0.6501	687
0.1702	443	0.5449	751	0.7084	624
0.1982	499	0.5624	748	0.7732	529
0.2483	578	0.5722	742	0.8111	460
0.2718	612	0.5885	735	0.8533	372
0.3074	660	0.5998	730	0.8915	284
0.3613	708	0.6022	727	0.9686	86
0.3973	730	0.6086	720		
0.4626	752	0.6124	717		
Ethyl Propanoate (1) + *tert*-Butanol (2)					
0.0345	76	0.4486	645	0.6458	600
0.0905	212	0.4998	648	0.7044	545
0.1495	331	0.5006	653	0.7533	487
0.1943	402	0.5163	652	0.8103	404
0.2497	482	0.5188	651	0.8580	325
0.2987	539	0.5569	647	0.9096	224
0.3496	577	0.5646	642	0.9432	154
0.3997	619	0.5964	631		
0.4466	639	0.6368	607		
Ethyl Butanoate (1) + *tert*-Butanol (2)					
0.0445	92	0.4468	609	0.7129	483
0.0966	208	0.4837	611	0.7538	433
0.1518	311	0.5015	611	0.7934	377
0.1999	383	0.5259	607	0.8465	299
0.2466	441	0.5538	599	0.9017	200
0.3111	513	0.6004	574	0.9614	82
0.3504	560	0.6399	550		
0.4043	591	0.6630	523		
T = 318.15 K					
Ethyl Methanoate (1) + *tert*-Butanol (2)					
0.1022	409	0.4934	919	0.6390	821
0.1289	486	0.5055	920	0.6902	760
0.2320	707	0.5111	919	0.7388	682
0.2909	796	0.5267	913	0.7922	579
0.3356	841	0.5360	909	0.8429	471
0.4076	897	0.5637	891	0.8913	345
0.4696	917	0.5859	875	0.9414	204
Ethyl Ethanoate (1) + *tert*-Butanol (2)					
0.0796	237	0.4344	786	0.7670	596
0.1377	370	0.4633	793	0.8516	418
0.1899	483	0.5377	795	0.8891	361
0.2558	614	0.5626	787	0.9294	237
0.2985	684	0.6284	755		
0.3703	744	0.6913	700		
Ethyl Propanoate (1) + *tert*-Butanol (2)					
0.0694	185	0.3648	616	0.7319	543
0.1223	299	0.4303	643	0.8088	445
0.1759	387	0.4669	650	0.8557	375
0.2144	451	0.5429	653	0.9183	228
0.2746	529	0.5960	643		
0.3188	579	0.6662	605		
Ethyl Butanoate (1) + *tert*-Butanol (2)					
0.0604	183	0.4477	644	0.6597	603
0.1099	285	0.4595	650	0.7011	573
0.1559	363	0.4778	653	0.7450	515
0.2141	445	0.4982	655	0.7968	450
0.2650	517	0.4996	656	0.8396	381
0.2982	541	0.5163	656	0.8701	315
0.3386	574	0.5222	655	0.9283	201
0.3900	614	0.5936	638		

Table 3. Excess Enthalpies H^E_m, for Binary Systems of Ethyl 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}
T = 299.15 K					
Ethyl Methanoate (1) + *tert*-Butanol (2)					
0.0689	587.9	0.4738	2166.3	0.7701	1606.6
0.1401	1064.7	0.5242	2163.9	0.8357	1258.5
0.2146	1481.9	0.5696	2155.9	0.8964	892.8
0.2869	1797.6	0.5710	2139.6	0.9485	453.1
0.3549	1999.3	0.6322	2044.0		
0.4172	2115.9	0.6996	1868.8		
Ethyl Ethanoate (1) + *tert*-Butanol (2)					
0.0546	376.1	0.4207	1862.1	0.6800	1727.0
0.1163	746.3	0.4707	1921.1	0.7438	1525.6
0.1810	1100.4	0.5157	1939.5	0.8091	1250.1
0.2456	1390.7	0.5541	1932.4	0.8769	887.2
0.3079	1610.9	0.5640	1925.7	0.9385	489.2
0.3672	1767.4	0.6199	1855.8		
Ethyl Propanoate (1) + *tert*-Butanol (2)					
0.0555	335.2	0.4164	1744.1	0.7300	1481.7
0.1332	766.9	0.4497	1789.5	0.8294	1076.0
0.2151	1134.8	0.4770	1808.5	0.9242	551.1
0.2979	1449.1	0.5513	1799.3		
0.3767	1662.9	0.6351	1722.9		
Ethyl Butanoate (1) + *tert*-Butanol (2)					
0.0438	251.8	0.3568	1549.4	0.6746	1596.1
0.0937	515.6	0.4053	1642.5	0.7522	1386.3
0.1461	778.9	0.4331	1696.6	0.8330	1050.1
0.1991	1040.6	0.4818	1741.8	0.9172	598.9
0.2541	1237.4	0.5387	1751.9		
0.3061	1411.9	0.6024	1711.3		
T = 318.15 K					
Ethyl Methanoate (1) + *tert*-Butanol (2)					
0.0612	520.5	0.4911	2048.0	0.7860	1546.7
0.1263	916.3	0.5110	2051.6	0.8292	1348.0
0.2016	1365.3	0.5304	2048.5	0.8754	1092.0
0.2725	1675.1	0.5696	2026.6	0.9191	805.4
0.3389	1854.9	0.6207	1986.9	0.9757	305.0
0.3986	1972.3	0.6806	1878.3		
0.4509	2030.7	0.7292	1744.0		
Ethyl Ethanoate (1) + *tert*-Butanol (2)					
0.0538	334.2	0.3987	1764.9	0.6844	1663.3
0.1146	687.7	0.4461	1833.7	0.7436	1470.8
0.1733	1004.7	0.4878	1862.5	0.8108	1194.0
0.2313	1285.3	0.5176	1873.0	0.8797	828.2
0.2953	1510.4	0.5676	1857.5	0.9442	433.3
0.3487	1658.2	0.6236	1793.9		
Ethyl Propanoate (1) + *tert*-Butanol (2)					
0.0510	292.6	0.4028	1654.3	0.6499	1665.9
0.1094	585.3	0.4347	1714.8	0.7164	1506.7
0.1681	875.1	0.4528	1738.2	0.7897	1255.3
0.2276	1132.5	0.4786	1773.9	0.8641	908.4
0.2892	1371.5	0.5297	1780.1	0.9381	479.0
0.3477	1536.8	0.5872	1752.5		
Ethyl Butanoate (1) + *tert*-Butanol (2)					
0.0394	293.3	0.3850	1574.8	0.5934	1714.0
0.0951	577.3	0.4267	1638.2	0.6595	1619.5
0.1580	850.7	0.4576	1690.5	0.7407	1405.9
0.2201	1088.2	0.4628	1694.3	0.8336	1040.4
0.2807	1310.1	0.4938	1723.2	0.9223	569.7
0.3377	1460.0	0.5386	1738.2		

versus temperature measurements were only made for *tert*-butyl alcohol in this case. The direct experimental values are given in Table 5, while Table 6 presents the constants in the Antoine equation,

$$\log(p_i^0/\text{kPa}) = A - B/[(T/K) - C] \qquad (2)$$

obtained by a least-squares method. Table 6 compares the experimental values for A, B, and C for *tert*-butyl alcohol with the literature values. The values used for the ethyl esters in this study also appear in the table. Figure 3 plots

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

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

binary mixture of *tert*-butanol (2) +	k_v	A_0	A_1	A_2	$10^9 s(V_m^E)$ / m^3·mol^{-1}
		$T = 303.15$ K			
+ethyl methanoate (1)	1.434	5796	−6988	4200	6
+ethyl ethanoate (1)	1.047	3264	−444		6
+ethyl propanoate (1)	1.555	3893	−3548	1478	4
+ethyl butanoate (1)	0.532	1235	1077	1757	5
		$T = 318.15$ K			
+ethyl methanoate (1)	0.603	3123	−1011	3614	5
+ethyl ethanoate (1)	1.597	5050	−5424	2856	8
+ethyl propanoate (1)	1.186	3378	−2461	1900	5
+ethyl butanoate (1)	0.634	2212	−1334	3629	5

$Y_m^E = H_m^E/RT$

binary mixture of *tert*-butanol (2) +	k_h	A_0^1	A_1^1	A_2^1	$10^3 s(H_m^E)$ / J·mol^{-1}
		$T = 299.15$ K			
+ethyl methanoate (1)	1.047	9598.6	−3204.1	2849.0	7.6
+ethyl ethanoate (1)	1.546	11080.1	−8830.9	3326.1	3.9
+ethyl propanoate (1)	0.864	5408.2	3533.5	5.9	8.3
+ethyl butanoate (1)	0.948	5700.3	2539.3	1.6	8.6
		$T = 318.15$ K			
+ethyl methanoate (1)	1.447	12667.8	−1437.4	10257.3	13.8
+ethyl ethanoate (1)	0.885	5921.1	3018.9	3.8	9.3
+ethyl propanoate (1)	0.872	5019.3	3952.1	−1.7	11.0
+ethyl butanoate (1)	0.591	4603.0	−2036.6	10288.1	11.3

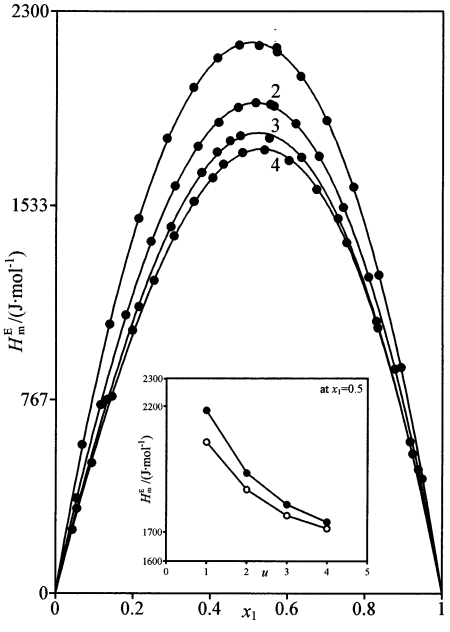

Figure 2. Experimental values (●) and correlation curves for H_m^E vs x_1 at 299.15 K for the binary mixtures $C_{u-1}H_{2u-1}COOC_2H_5$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2); labels indicate the *u* values; the inset figure shows the changes in equimolar enthalpies for different values of *u* and at two temperatures, 303.15 K (●) and 318.15 K (○).

the vapor pressure curves for the components, that is, the ethyl esters and the *tert*-butyl alcohol, on reduced coordinates employing an equation similar to eq 2 to correlate the nondimensional temperatures and vapor pressures (see Ortega et al.[16]), representing the constants in lower case (*a*, *b*, and *c*). These values can be related quite readily to the values in eq 2 and have also been presented in Table 6 together with the acentric factors *ω*, as defined by Pitzer,

Table 5. Experimental Vapor Pressures, p_i^0, for *tert*-Butanol

*T*K	p_i^0/kPa	*T*K	p_i^0/kPa	*T*K	p_i^0/kPa
332.30	37.40	348.90	77.42	359.27	117.00
333.03	38.69	349.34	78.76	359.84	119.53
333.45	39.34	349.74	80.07	360.13	120.87
334.60	41.37	350.10	81.30	360.46	122.36
335.29	42.93	350.53	82.71	360.64	123.08
335.87	43.85	350.90	83.96	360.97	124.73
336.43	45.01	351.33	85.66	361.26	126.15
337.17	46.69	351.67	86.64	361.47	126.96
337.80	48.06	352.05	88.15	361.73	128.20
338.37	49.27	352.45	89.39	362.02	129.63
338.86	50.27	352.80	90.67	362.54	132.15
339.50	51.81	353.13	92.07	362.75	133.36
340.08	53.17	353.50	93.39	363.03	134.71
340.59	54.25	353.81	94.63	363.08	134.81
341.17	55.83	354.18	95.95	363.56	137.40
341.63	56.78	354.51	97.04	363.82	138.80
342.18	58.37	354.85	98.36	364.09	140.03
342.68	59.61	355.23	100.07	364.33	141.29
343.13	60.61	355.50	100.88	364.66	142.96
343.70	62.30	355.58	101.32	365.09	145.34
344.13	63.27	355.83	102.22	365.27	146.36
344.68	64.99	356.22	103.92	365.62	148.18
345.06	65.81	356.52	105.27	366.10	150.66
345.49	67.05	356.86	106.62	366.51	153.08
346.11	69.05	357.15	107.71	366.81	154.69
346.51	70.21	357.45	109.12	367.08	156.16
346.83	71.11	357.77	110.47	367.49	158.58
347.28	72.45	358.06	111.51	367.83	160.39
347.68	73.43	358.35	112.83	368.23	162.82
348.20	75.35	358.68	114.36		
348.54	76.17	358.96	115.48		

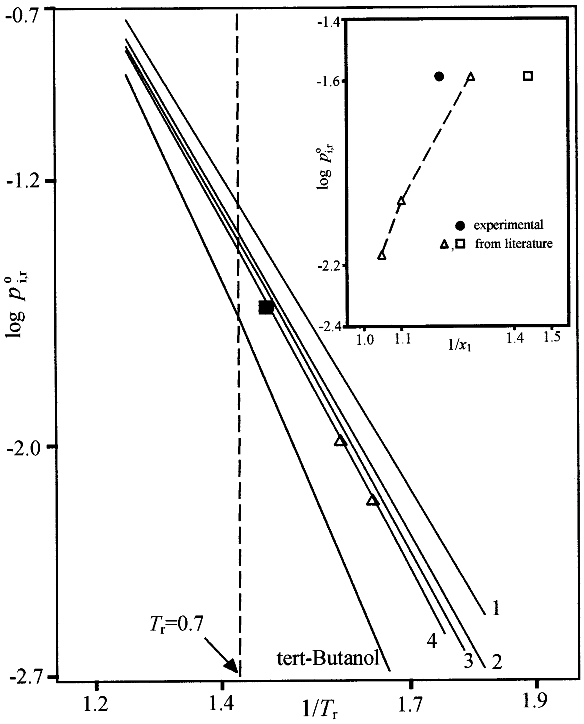

Figure 3. Vapor pressure curves plotted on reduced coordinates for the ethyl esters $C_{u-1}H_{2u-1}COOC_2H_5$ and *tert*-butyl alcohol calculated using the coefficient values set out in Table 6 and the experimental (●) and literature (ref 21) (△, □) azeotropic points; labels indicate the *u* values; the inset figure shows the same azeotropic points as a function of ester concentration.

calculated for each of the components, which were used in the subsequent characterization of the VLE values. There was acceptable agreement between the *ω* values obtained and the literature values.

Table 6. Coefficients of the Antoine Equation

Coefficients *A*, *B*, and *C* of the Antoine Equation[a] Used in This Work with Expression of Temperature Range

compound	A	B	C	$s(p_i^0)^c$/kPa	ΔT/K	references
tert-butanol	6.600 44	1238.69	85.99	0.09	330−370	this work
	6.356 48	1107.06	101.05			Riddick et al. (ref 10)
	6.328 30	1092.97	102.65		330−365	Boublik et al. (ref 15)
ethyl methanoate	6.650 74	1431.31	19.09		300−350	Soto et al. (ref 3)
ethyl ethanoate	6.596 55	1480.71	27.61		300−370	Hernández et al. (ref 14)
ethyl propanoate	6.301 80	1382.89	50.09		340−390	Hernández et al. (ref 14)
ethyl butanoate	6.363 64	1496.03	50.90		370−410	Hernández et al. (ref 14)

Coefficients *a*, *b*, and *c* of the Antoine Equation in Reduced Form,[b] Calculated from Experimental Vapor Pressures, and the Acentric Factor for Each of the Compounds

compound	a	b	c	ω	references
tert-butanol	2.998 37	2.443 89	0.170	0.6136	calculated[b]
				0.6158	Daubert and Danner (ref 11)
ethyl methanoate	2.953 55	2.789 68	0.040	0.2732	calculated[b]
				0.2849	Daubert and Danner (ref 11)
ethyl ethanoate	3.019 07	2.836 59	0.052	0.3584	calculated[b]
				0.3611	Daubert and Danner (ref 11)
ethyl propanoate	2.758 52	2.513 25	0.093	0.3819	calculated[b]
				0.3944	Daubert and Danner (ref 11)
ethyl butanoate	2.842 11	2.577 48	0.094	0.4111	calculated[b]
				0.4190	Daubert and Danner (ref 11)

[a] $\log(p_i^0/\mathrm{kPa}) = A - B/[T/(\mathrm{K}) - C]$. [b] $\log(p_{i,\mathrm{r}}^0) = a - b/(T_\mathrm{r} - c)$. [c] Standard deviation, *s*, between the experimental values and the corresponding fitting curve.

Presentation of VLE Values. The $T-x_1-y_1$ values were determined on reaching the equilibrium states between the liquid and vapor phases at the working pressure of $p = (101.32 \pm 0.02)$ kPa for the four binary mixtures, represented empirically as $H_{2u-1}C_{u-1}COOC_2H_5$ (u = 1 to 4) (1) + $CH_3(CH_3)C(OH)CH_3$ (2). Considering that the vapor phase was not ideal, the activity coefficients for the components in the liquid phase were calculated by

$$\ln \gamma_i = \ln\left(\frac{py_i}{p_i^0 x_i}\right) + \frac{(B_{ii} - V_i^0)(p - p_i^0)}{RT} + \frac{p}{RT}\sum_j \sum_k y_j y_k (2\delta_{ji} - \delta_{jk}) \quad (3)$$

where

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

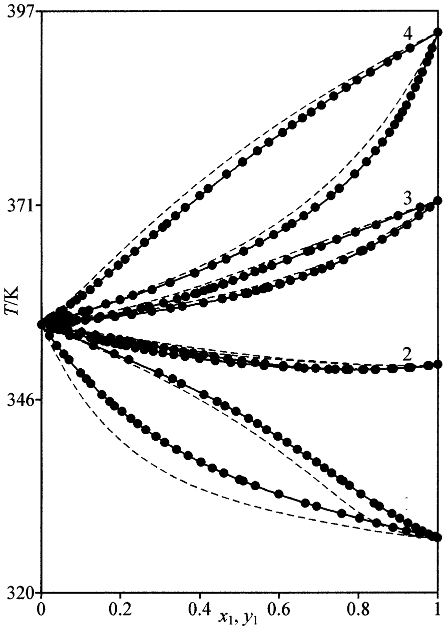

Figure 4. Representation of experimental VLE values (●) and correlation curves for T vs x_1,y_1 for the binary mixtures $C_{u-1}H_{2u-1}$-$COOC_2H_5$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2); labels indicate the *u* values. Dashed lines indicate curves estimated using the UNIFAC model (ref 5).

where the second virial coefficients, B_{ij}, for the pure components and for the mixtures were calculated using the correlations proposed by Tsonopoulos.[17] The molar volume, B_{ij}, for pure component *i* at each equilibrium temperature was calculated using the Rackett equation as modified by Spencer and Danner[18] with the Z_{RA} coefficients as published by Reid et al.[19] The activity coefficients obtained using eq 3 were used to calculate the values for the nondimensional Gibbs function G_m^E/RT, and the results for each of the binary systems appear in Table 7. The version of the point-to-point consistency test proposed by Fredenslund et al.[20] was applied to the results, and for the vapor phase the discrepancies between the experimental mole fractions and the values calculated by the model were assessed for each equilibrium state. The experimental values in Table 7 satisfied the condition $\bar{\delta} = \sum_i(y_{i,\mathrm{exp}} - y_{i,\mathrm{cal}})/N \leq 0.01$. Figure 4 plots T versus x_1,y_1 for the four systems of an ethyl ester (1) + *tert*-butyl alcohol (2). As already mentioned in the Introduction, the literature does not contain VLE values for the systems considered here that can be used for comparison. Setting $(y_1 - x_1) = 0$ and $(\mathrm{d}T/\mathrm{d}x)_p = 0$, the azeotropic point observed for the system composed of *x* ethyl ethanoate + (1 − *x*) *tert*-butyl alcohol was calculated to occur at $x_{az} = 0.832$ and $T_{az} = 349.59$ K. Figure 3 shows the azeotropic point found in this study along with published values[1,21] for this same binary system under other experimental conditions. The plot has been performed on reduced coordinates, taking the geometric mean for the critical quantities of the pure substances as the mixing rule for calculating the pseudocritical quantities. While the plot of the $p_{i,\mathrm{r}}^0$ versus $1/T_\mathrm{r}$ values yielded a good correlation with the azeotropic line, the inset figure reveals a sizable discrepancy in the azeotrope concentration. Future work may provide clarification of this finding.

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

T/K	x_1	y_1	γ_1	γ_2	G_m^E/RT	T/K	x_1	y_1	γ_1	γ_2	G_m^E/RT	T/K	x_1	y_1	γ_1	γ_2	G_m^E/RT
Ethyl Methanoate (1) + *tert*-Butanol (2)																	
354.13	0.0197	0.0712	1.606	1.001	0.010	342.41	0.2433	0.5452	1.391	1.012	0.089	333.05	0.5994	0.8066	1.114	1.220	0.144
352.79	0.0380	0.1306	1.584	1.004	0.022	341.62	0.2637	0.5679	1.368	1.021	0.098	331.85	0.6664	0.8393	1.083	1.285	0.137
351.69	0.0559	0.1837	1.562	1.003	0.027	340.71	0.2889	0.5964	1.348	1.026	0.105	331.45	0.6941	0.8525	1.070	1.310	0.130
350.93	0.0694	0.2210	1.546	1.000	0.030	339.95	0.3116	0.6194	1.328	1.033	0.110	330.50	0.7579	0.8842	1.048	1.358	0.110
349.21	0.0989	0.2961	1.525	0.998	0.040	339.02	0.3409	0.6460	1.302	1.044	0.118	329.85	0.8025	0.9044	1.034	1.416	0.095
348.40	0.1136	0.3303	1.516	0.997	0.044	338.18	0.3704	0.6702	1.276	1.055	0.124	329.23	0.8464	0.9246	1.023	1.478	0.079
347.77	0.1245	0.3530	1.505	1.000	0.051	337.30	0.4025	0.6939	1.249	1.072	0.131	328.66	0.8880	0.9443	1.014	1.538	0.061
346.30	0.1528	0.4097	1.485	1.000	0.060	336.55	0.4314	0.7143	1.228	1.087	0.136	328.20	0.9216	0.9611	1.010	1.568	0.044
345.38	0.1720	0.4427	1.464	1.003	0.068	335.87	0.4599	0.7318	1.205	1.107	0.141	327.78	0.9544	0.9773	1.005	1.604	0.027
344.80	0.1843	0.4626	1.452	1.005	0.073	335.01	0.4990	0.7555	1.178	1.130	0.143	327.44	0.9868	0.9933	1.000	1.662	0.006
344.04	0.2037	0.4907	1.425	1.006	0.077	334.79	0.5095	0.7611	1.170	1.138	0.144						
343.10	0.2258	0.5224	1.407	1.009	0.084	334.19	0.5396	0.7770	1.150	1.163	0.145						
Ethyl Ethanoate (1) + *tert*-Butanol (2)																	
355.18	0.0234	0.0358	1.313	1.002	0.009	352.77	0.2139	0.2834	1.223	1.014	0.054	350.14	0.5619	0.6104	1.087	1.096	0.087
355.06	0.0334	0.0508	1.310	1.001	0.010	352.52	0.2369	0.3086	1.211	1.018	0.059	349.97	0.6098	0.6478	1.068	1.120	0.084
354.90	0.0447	0.0671	1.299	1.002	0.013	352.27	0.2599	0.3339	1.204	1.021	0.063	349.81	0.6629	0.6913	1.054	1.143	0.080
354.57	0.0686	0.1012	1.289	1.002	0.020	352.05	0.2823	0.3571	1.193	1.024	0.067	349.68	0.7244	0.7416	1.039	1.177	0.072
354.21	0.0947	0.1367	1.275	1.004	0.027	351.84	0.3063	0.3821	1.184	1.027	0.070	349.63	0.7679	0.7759	1.027	1.214	0.065
353.88	0.1235	0.1742	1.259	1.005	0.032	351.60	0.3339	0.4091	1.172	1.032	0.074	349.60	0.8102	0.8129	1.021	1.241	0.058
353.61	0.1417	0.1969	1.250	1.008	0.038	351.36	0.3625	0.4361	1.159	1.039	0.078	349.59	0.8428	0.8415	1.016	1.270	0.051
353.41	0.1573	0.2161	1.243	1.010	0.042	351.08	0.3991	0.4701	1.145	1.047	0.082	349.74	0.8878	0.8823	1.007	1.314	0.036
353.30	0.1668	0.2281	1.242	1.010	0.044	350.81	0.4386	0.5056	1.130	1.057	0.085	349.88	0.9322	0.9252	1.001	1.374	0.022
353.08	0.1857	0.2501	1.231	1.012	0.049	350.58	0.4771	0.5384	1.114	1.069	0.086	350.10	0.9778	0.9744	0.998	1.424	0.006
352.91	0.2009	0.2682	1.227	1.013	0.052	350.41	0.5052	0.5635	1.107	1.075	0.087						
Ethyl Propanoate (1) + *tert*-Butanol (2)																	
355.80	0.0261	0.0218	1.377	0.996	0.005	359.27	0.4845	0.3645	1.109	1.076	0.088	363.36	0.7285	0.5811	1.034	1.163	0.065
355.88	0.0458	0.0378	1.357	0.997	0.011	359.64	0.5141	0.3871	1.097	1.086	0.088	364.11	0.7628	0.6200	1.029	1.176	0.061
355.96	0.0784	0.0641	1.341	1.001	0.024	359.73	0.5212	0.3926	1.094	1.089	0.088	365.24	0.8056	0.6711	1.019	1.195	0.050
356.19	0.1102	0.0896	1.323	1.000	0.031	360.01	0.5421	0.4091	1.086	1.096	0.087	365.38	0.8115	0.6790	1.019	1.197	0.049
356.38	0.1423	0.1147	1.304	1.002	0.039	360.28	0.5598	0.4239	1.081	1.101	0.086	365.91	0.8316	0.7055	1.017	1.207	0.045
356.63	0.1865	0.1485	1.277	1.007	0.051	360.49	0.5739	0.4357	1.076	1.106	0.085	366.79	0.8600	0.7456	1.012	1.216	0.037
356.89	0.2279	0.1786	1.247	1.013	0.060	360.91	0.6005	0.4573	1.066	1.117	0.082	367.73	0.8910	0.7921	1.008	1.236	0.031
357.31	0.2791	0.2170	1.220	1.018	0.069	360.97	0.6033	0.4604	1.066	1.116	0.082	368.72	0.9220	0.8444	1.009	1.251	0.025
357.75	0.3259	0.2517	1.195	1.024	0.074	361.39	0.6289	0.4832	1.059	1.126	0.080	369.94	0.9522	0.8996	1.003	1.264	0.014
357.99	0.3552	0.2710	1.171	1.034	0.078	361.96	0.6597	0.5112	1.049	1.138	0.076	371.05	0.9797	0.9552	1.002	1.280	0.007
358.46	0.4088	0.3082	1.140	1.052	0.084	362.51	0.6885	0.5394	1.043	1.149	0.072						
358.94	0.4565	0.3424	1.117	1.069	0.087	362.93	0.7081	0.5592	1.037	1.156	0.068						
Ethyl Butanoate (1) + *tert*-Butanol (2)																	
355.90	0.0218	0.0098	1.498	1.000	0.009	364.21	0.4661	0.2113	1.134	1.081	0.100	379.66	0.8600	0.5739	1.018	1.338	0.056
356.38	0.0454	0.0204	1.472	0.996	0.014	365.28	0.5106	0.2352	1.112	1.101	0.101	380.98	0.8784	0.6082	1.015	1.361	0.050
356.54	0.0555	0.0250	1.467	0.996	0.017	366.42	0.5503	0.2602	1.098	1.115	0.101	381.96	0.8901	0.6326	1.011	1.370	0.044
356.71	0.0690	0.0310	1.455	0.998	0.024	367.45	0.5856	0.2835	1.087	1.131	0.100	382.86	0.9013	0.6579	1.011	1.382	0.042
357.31	0.1040	0.0470	1.433	0.997	0.035	368.42	0.6169	0.3055	1.077	1.147	0.098	383.63	0.9105	0.6800	1.011	1.393	0.040
357.49	0.1201	0.0541	1.419	1.001	0.043	368.91	0.6322	0.3165	1.072	1.157	0.097	384.54	0.9204	0.7058	1.010	1.402	0.036
358.32	0.1628	0.0735	1.382	1.000	0.052	369.93	0.6619	0.3384	1.059	1.177	0.093	385.74	0.9320	0.7369	1.006	1.416	0.029
358.85	0.1983	0.0887	1.344	1.007	0.064	371.03	0.6908	0.3632	1.051	1.194	0.089	386.87	0.9424	0.7685	1.004	1.423	0.024
359.44	0.2309	0.1032	1.315	1.011	0.072	372.63	0.7301	0.3993	1.038	1.224	0.082	387.84	0.9510	0.7961	1.002	1.432	0.019
360.20	0.2797	0.1231	1.262	1.027	0.084	373.55	0.7514	0.4207	1.032	1.244	0.078	388.93	0.9606	0.8295	1.001	1.443	0.016
361.13	0.3246	0.1431	1.224	1.035	0.089	375.45	0.7901	0.4666	1.026	1.276	0.071	390.22	0.9720	0.8731	1.004	1.457	0.014
362.37	0.3871	0.1704	1.172	1.057	0.095	377.06	0.8195	0.5076	1.023	1.301	0.066	391.06	0.9780	0.8975	1.002	1.462	0.010
363.43	0.4312	0.1939	1.155	1.066	0.098	378.52	0.8425	0.5441	1.020	1.319	0.060	392.07	0.9855	0.9299	1.001	1.475	0.007

Processing of the VLE Data. Isobaric VLE values were correlated using an equation which contained the product $z_1z_2 \equiv z(1 - z)$ instead of $x_1x_2 \equiv x(1 - x)$ as was done in a previous study,[3] with z being defined as in eq 1 for a binary mixture. When correlating the values of the nondimensional Gibbs function, this equation took the form

$$\frac{G_m^E}{RT}(T,x_1) = z_1z_2\sum_{i=0}^{m}A_iz_1{}^i \tag{4}$$

with the A_i coefficients being treated as temperature-dependent by means of the relation

$$A_i = A_{i1}T + \frac{A_{i2}}{T} + A_{i3} \tag{5}$$

derived from taking thermal capacity to be a linear function of temperature, $C_p^E = a + bT$. From the following fundamental thermodynamic relations,

$$C_p^E = \left(\frac{\partial H_m^E}{\partial T}\right)_{p,x} \qquad -\frac{H_m^E}{RT} = T\left[\frac{\partial(G_m^E/RT)}{\partial T}\right]_{p,x} \tag{6}$$

the excess Gibbs energy function can be written as

$$\frac{G_m^E}{RT} = -a\ln T - \frac{b}{2}T + \frac{I_1}{T} + I_2 \tag{7}$$

where I_1 and I_2 are the corresponding integration constants. Furthermore, on replacement of the term ln T in a power series of $(T - h)$ where $h > 0$, truncated after the first term, eq 7 becomes

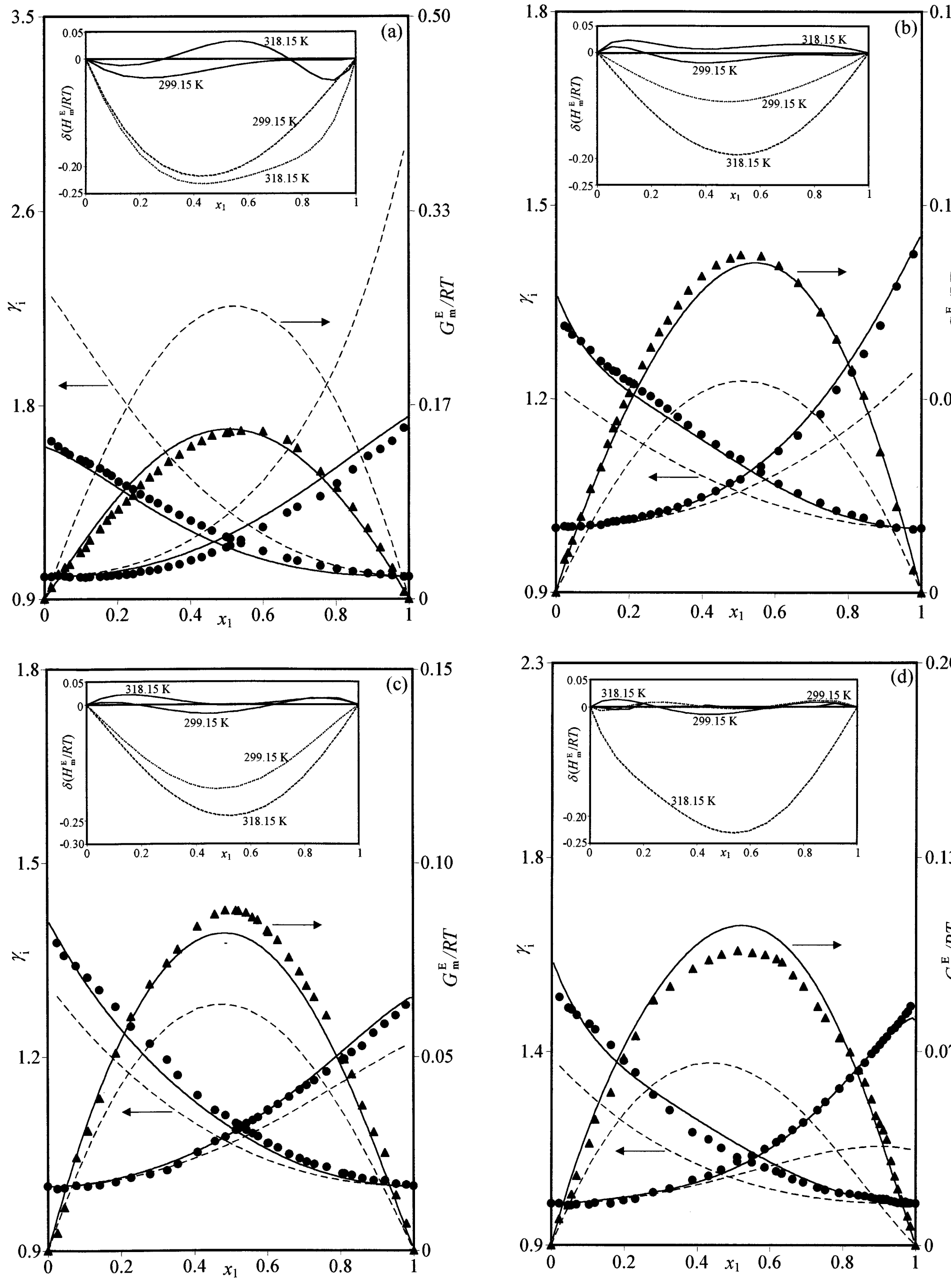

Figure 5. (a−d) Experimental and correlated curves using eq 11 (solid lines) for the quantities G_m^E vs x_1 (▲) and γ_i vs x_1 (●) for the binary mixtures $C_{u-1}H_{2u-1}COOC_2H_5$ (1) + $CH_3(CH_3)C(OH)CH_3$ (2). Dashes lines indicate curves obtained using the UNIFAC model (ref 5); (a) $u = 1$; (b) $u = 2$; (c) $u = 3$; (d) $u = 4$; the inset figures show the deviations in $\delta H_m^E/RT$ obtained as the difference between the curve calculated by the UNIFAC model (ref 5) (dashed lines) or by correlation of the VLE values using eqs 6 and 11 (solid lines) and the corresponding direct experimental fit, eq 1.

$$\frac{G_m^E}{RT} = -\frac{a}{h}T - a(\ln h - 1) - \frac{b}{2}T + \frac{I_1}{T} + I_2 = -\left(\frac{a}{h} + \frac{b}{2}\right)T + \frac{I_1}{T} + I_2 - a(\ln h - 1) \quad (8)$$

which can be compared to eq 5 and which could also have been obtained by taking thermal capacity to be constant with respect to temperature over short temperature intervals.

Nevertheless, this approach yields a model with too many parameters. One way to reduce it is to hold C_p^E constant with respect to temperature. This yields an expression for the Gibbs function,

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

Even so, unnecessary parametrization was observed on developing eq 9 as a polynomial in z. To avoid this, only the even-powered terms for z, that is, terms for which $i = 0, 2, 4, \ldots$, were considered.

Setting $m = 2$, eq 9 was used here to correlate the isobaric VLE data sets, namely, $\{T_j, x_{1j}, \ln \gamma_{1j}, \ln \gamma_{2j}); j = 1, \ldots, n\}$ on one hand and $\{x_{1i}, (H_m^E/RT_i)_i); i = 1, \ldots, q\}$ on the other, where $\ln \gamma_{1j}$ and $\ln \gamma_{2j}$ were the natural logarithms of the activity coefficients obtained for the concentration of the first component, x_{1j}, at temperature T_j, and the nondimensional quantities $(H_m^E/RT_i)_i$ were the

Table 8. Parameters Obtained in the Correlation of VLE Data Using Equation 11; in Parentheses is the Correlation Coefficient, r^2

	mixtures[a]			
parameters	1	2	3	4
A_{01}	983.112	656.455	791.713	652.957
A_{02}	−2.311	−1.637	−1.886	−1.470
A_{21}	176.530	818.248	240.027	591.678
A_{22}	−0.687	−2.013	−0.626	−1.217
k_g	0.989	0.671	0.985	0.789
$s(G^E_m/RT)$	0.007 (0.98)	0.002 (0.97)	0.004 (0.97)	0.005 (0.98)
$s(\gamma_i)$	0.037 (0.98)	0.010 (0.99)	0.011 (0.99)	0.013 (0.99)
$s(H^E_m/RT)$ at 299.15 K	0.020 (0.99)	0.012 (0.99)	0.013 (0.99)	0.011 (0.99)
$s(H^E_m/RT)$ at 318.15 K	0.024 (0.99)	0.014 (0.99)	0.012 (0.99)	0.007 (0.99)

[a] Columns: 1, ethyl methanoate (1) + *tert*-butanol (2); 2, ethyl ethanoate (1) + *tert*-butanol (2); 3, ethyl propanoate (1) + *tert*-butanol (2); and 4, ethyl butanoate (1) + *tert*-butanol (2).

excess enthalpies measured at a concentration of the reference component, that is, the first component, x_{1i}, at temperature T_i, which were typically other than the equilibrium values. The subscripts i and j correspond to the measurement number in question for the activity coefficients and for the excess enthalpies, respectively.

For application of the least-squares procedure, an objective function that would reveal the discrepancies observed between the experimental values and the estimates for an equilibrium state, that is, at equal concentration, temperature, and pressure values, produced by the model was used. The objective function, OF, thus took the form

$$\mathrm{OF} = \sum_{i=1}^{q}\left[\frac{H^E_m}{RT}(T_i,x_{1i}) - \left(\frac{H^E_m}{RT_i}\right)_i\right]^2 + \sum_{j=1}^{n}[\ln \gamma_1(T_j,x_{1j}) - \ln \gamma_{1j}]^2 + \sum_{j=1}^{n}[\ln \gamma_2(T_j,x_{1j}) - \ln \gamma_{2j}]^2 \qquad (10)$$

and the function variables were the coefficients from eq 9 for the Gibbs function, the optimum values being the values that minimized the OF. However, the Gibbs function values, which were calculated from the natural logarithms of the activity coefficients, γ_i, and thus did not provide any independent statistical information, were not used directly in the OF.

The possibility that the OF might be nonconvex and thus might have different local extremes, together with the complicated handling of nonlinear systems of equations, caused us to choose a genetic algorithm for optimization of the OF.

Table 8 presents the estimated values of the model parameters together with the values for the measures of goodness of fit, s and r^2. Figure 5a−d depicts the calculated curves together with the experimental equilibrium values and the observed differences between the enthalpies obtained using eqs 9 and 6 and the experimental values at the two working temperatures employed in this study. The values of s and r^2 obtained for each of the systems are indicative of good correlations and thus that this approach is appropriate for use in this and future studies.

Conclusions

This work presents VLE values at 101.32 kPa and the excess molar quantities H^E_m and V^E_m at two working temperatures for four binary systems consisting of an ethyl ester (methanoate to butanoate) and *tert*-butyl alcohol. The VLE measurements were thermodynamically consistent, according to a point-to-point test. An equation and corresponding procedure intended to improve processing of VLE data for binary systems was employed, based on a new polynomial expression for the nondimensional Gibbs function related to mixture component concentration by the so-called active fraction and temperature. The most suitable final expression was

$$\frac{G^E_m}{RT}(T,x_1) = z_1(x_1)[1 - z_1(x_1)]\left[\left(\frac{A_{01}}{T} + A_{02}\right) + \left(\frac{A_{21}}{T} + A_{22}\right)z_1^{\,2}(x_1)\right] \qquad (11)$$

The coefficients for eq 11 were estimated based on the activity coefficient and mixing enthalpies using a method of least squares and a genetic algorithm for optimization of the objective function, eq 10. Application of the model yielded excellent results for the set of four binary mixtures composed of an ethyl ester + *tert*-butyl alcohol; hence the equation and procedure employed would appear to be suitable for use in processing VLE data in future studies. Additionally, as had been done in earlier studies on systems containing isobutanol,[3,14] the model put forward by Gmehling et al.[5] was also used to predict the VLE and enthalpies, but with the current parameters the model does not seem to be appropriate for use with a tertiary alkanol (see Figures 4 and 5a−d), even though it gives special treatment to this type of alkanol, in that it yielded large discrepancies for the Gibbs function, whose estimated values were considerably higher than the experimental values for the mixture containing ethyl methanoate but conversely lower for the other three mixtures.

Nomenclature

A, B, C = parameters of Antoine's equation
B_{ij} = second virial coefficients
k = parameter of eqs 1, 4, and 9
N = number of experimental points
H^E_m = excess enthalpy
G^E_m = excess Gibbs function
p = absolute pressure
p^0_i = vapor pressure
R = gas constant
r^2 = correlation coefficient on Y-function, $r^2 = \sum(Y_{cal} - \bar{Y})^2/[\sum(Y_{cal} - \bar{Y})^2 + \sum(Y_{cal} - Y_{exp})^2]$
s = standard deviation on Y-function, $s = [\sum(Y_{exp} - Y_{cal})^2/(N - n)]^{1/2}$
T = temperature
V^E_m = excess volume
x_i = liquid mole fraction
y_i = vapor mole fraction
z_i = active fraction of i defined by eq 1
γ_i = activity coefficient of i
ω = acentric factor

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