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 $H_{\rm m}^{\rm E}$ and $V_{\rm m}^{\rm E}$ 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 $H_{\rm m}^{\rm E}$ 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 (tertbutyl 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 $V_{\rm m}^{\rm E}$ 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 algorithm⁴ was used to fit the VLE and $H_{\rm m}^{\rm E}$ values simultaneously. Last, the suitability of the modified-UNIFAC⁵ 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.

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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 $n_{\rm D}$, which were used for purposes of comparison. The tert-butyl alcohol has a melting temperature⁹ 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 $\pm 2 \times 10^{-9}$ m³·mol⁻¹. Accord-

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

		$T_{\rm b,}^0/{ m K}$		ρ (298.15	K)∕kg•m ^{−3}	<i>n</i> _D (303.15 K)	
compound	mass fraction	expt	lit	expt	lit	expt	lit
<i>tert</i> -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_m^E , 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_m^E 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_m^E) were correlated using a modified version of an equation employed previously,³ of the form

$$Y_{\rm m}^{\rm E} = z_1 z_2 \sum_{i=0}^{m} A_i z_1^{\ i} \tag{1}$$

where

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

with $Y_{\rm m}^{\rm E}$ being a generic excess property and where for the volumes, *k* was set equal to $k_{\rm v} = V_2^{\theta}/V_1^{\theta}$, with V_i^{θ} 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, $s(V_m^E)$, 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 $V_{\rm m}^{\rm E}$ values with ester chain length and temperature, yielding the positive quantity $(\partial V_{\rm m}^{\rm E}/\partial T)_{p,x} > 0$. 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 , $H_{\rm m}^{\rm E}/RT$) using the same procedure mentioned above to optimize eq 1 yielded values of k, now designated $k_{\rm h}$, by



Figure 1. Experimental values (•) and correlation curves for V_m^E vs x_1 at 303.15 K for the binary mixtures $C_{u-1}H_{2u-1}COOC_2H_5$ (1) + CH₃(CH₃)C(OH)CH₃ (2); labels indicate the *u* values. \Box , 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 (\bigcirc).

iteration with a view to achieving the best fit. Table 4 lists the coefficients obtained for the correlations and the corresponding standard deviations, $s(H_m^E)$. 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 $(\partial H_m^E/\partial T)_{p,x}$ is negative in this case.

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_i^0) 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_m^E , for Binary Systems of Ethyl Esters (1) + *tert*-Butanol (2) at Two Different Temperatures

$10^{9} V_{\rm m}^{\rm E}$ $10^9 V_{\rm m}^{\rm E}$ $10^9 V_{\rm m}^{\rm E}$ m³·mol⁻¹ m³·mol⁻¹ m³⋅mol⁻¹ X_1 *X*1 X_1 T = 303.15 KEthyl 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 0.6956 742 0.4445 875 0.1973 607 0.4964 879 0.7432 659 0.2481 702 0.5013 880 0.8016 554 878 0.2631 732 0.5084 0.8477 463 790 0.5344 870 0.9067 0.3042 328 0.3255 810 0.5515 864 0.9465 217 0.3448 830 0.5677 858 Ethyl Et hanoate (1) + tert-Butanol (2) 0.0458 755 706 114 0.51780.63360.0972 265 0.5274 754 0.6501 687 0.1702 443 0.5449 751 0.7084 624 529 0.1982499 0.5624 748 0.7732 0.2483 578 0.5722 742 0.8111 460 0.2718 612 0.5885 735 0.8533 372 0.8915 0.3074 660 0.5998 730 284 0.3613 708 0.6022 727 0.9686 86 0.3973 730 0.6086 720 752 0.4626 0.6124 717 Ethyl Propanoate (1) + tert-Butanol (2) 0.0345 600 76 0.4486 0.6458 645 0.0905 212 0.7044 0.4998 648 545 0.1495 331 0.5006 653 0.7533 487 402 652 0.8103 404 0.1943 0.5163 0.2497 482 0.5188 651 0.8580 325 0.2987 539 0.5569 647 0.9096 224 577 642 154 0.3496 0.5646 0.9432 0.3997 619 0.5964 631 0.4466 639 0.6368 607 + tert-Butanol (2) Ethyl Butanoate (1) 0.0445 92 0.4468 609 0.7129 483 0.0966 208 0.4837 611 0.7538 433 377 0.1518 311 0.5015 611 0.79340.1999 383 0.5259 607 0.8465 299 0.2466 441 0.5538 599 0.9017 200 574 0.3111 513 0.6004 0.9614 82 0.3504 560 0.6399 550 0.4043 591 0.6630 523 T = 318.15 KEthyl Methanoate (1) + tert-Butanol (2)0.1022 **40**9 0.4934 919 0.6390 821 0.1289 486 0.5055 920 0.6902 760 0.7388 682 0.2320 707 0.5111 919 0.2909 796 0.5267 913 0.7922 579 0.3356 841 0.5360 909 0.8429 471 0.8913 0.4076 897 0.5637 891 345 0.4696 917 0.5859 875 0.9414 204 Ethyl Ethanoate (1) + tert-Butanol (2) 0.0796 596 237 0.4344 786 0.7670 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 744 700 0.6913 Ethyl Pr opanoate (1) + tert-Butanol (2) 0.0694 543 185 0.3648 616 0.7319 0.8088 0.1223 299 0.4303 643 445 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) 603 0.0604 183 0.4477 644 0.6597 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 0.8396 381 656 0.2982 0.5163 656 0.8701 541 315 0.3386 574 0.5222 655 0.9283 201 0.3900 614 0.5936 638

Table 3. Excess Enthalpies H_{m}^{E} , for Binary Systems of Ethyl Esters (1) + *tert*-Butanol (2) at Two Different Temperatures

_					
	$H_{\rm m}^{\rm E}$		$H_{\rm m}^{\rm E}$		$H_{ m m}^{ m E}$
<i>X</i> 1	J·mol ⁻¹	<i>X</i> 1	J·mol ⁻¹	<i>X</i> 1	J·mol ⁻¹
	0 11101	T = 90	0 15 17		0 11101
	Ethyl M	I = 28	(9.13 K)	itanol (2)	
0.0680	587.0	0 4738	$1) + le_1 - Dl 2166 3$	0.7701	1606 6
0.0003	1064 7	0.4738	2163.9	0.8357	1258 5
0.1401	1481 9	0.5696	2155.9	0.8964	892.8
0.22140	1797.6	0.5050	2139.6	0.0304	453 1
0.3549	1999.3	0.6322	2044 0	0.0400	455.1
0.4172	2115.9	0.6996	1868.8		
0.1172	Ethyl E	thanoate (1) + tert-Bu	tanol (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 Pı	opanoate (I) + tert-Bu	ıtanol (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 B	utanoate (1) + tert-Bu	tanol (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 = 31	8.15 K		
	Ethyl M	ethanoate (1) + tert-Bu	ıtanol (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 E	thanoate (1) + tert-Bu	tanol (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 Pı	ropanoate (1) + <i>tert</i> -Bu	itanol (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	1.0	
0.0004	Ethyl B	utanoate (1) + tert-Bu	tanol (2)	17140
0.0394	293.3	0.3850	15/4.8	0.5934	1/14.0
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,

$$\log(p_i^0/kPa) = A - B/[(T/K) - C]$$
(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, $V_{\rm m}^{\rm E}$ and $H_{\rm m}^{\rm E}/RT$

$Y_{\rm m}^{\rm E} = 10^9 V_{\rm m}^{\rm E}$ in (m ³ ·mol ⁻¹)									
binary mixture of					$10^9 s(V_{\rm m}^{\rm E})$				
<i>tert</i> -butanol (2) +	<i>k</i> _v	A_0	A_1	A_2	m³∙mol ^{−1}				
	T=	= 303.15	K						
+ethyl methanoate (1)	1.43	4 5796	-6988	4200	6				
+ethyl ethanoate (1)	1.04	7 3264	-444		6				
+ethyl propanoate (1)	1.55	5 3893	-3548	1478	4				
+ethyl butanoate (1)	0.53	2 1235	1077	1757	5				
	T=	= 318.15	К						
+ethyl methanoate (1)	0.60	3 3123	-1011	3614	5				
+ethyl ethanoate (1)	1.59	7 5050	-5424	2856	8				
+ethyl propanoate (1)	1.18	6 3378	-2461	1900	5				
+ethyl butanoate (1)	0.63	4 2212	-1334	3629	5				
	$Y_{\rm m}^{\rm E}$	$=H_{\rm m}^{\rm E}/R$	Т						
hinom mintune of					$10^3 s(H_{\rm m}^{\rm E})$				
<i>tert</i> -butanol (2) +	$k_{ m h}$	A_0^1	A_1^1	A_2^1	J·mol ⁻¹				
	<i>T</i> =	= 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				
5	T=	= 318.15	к						
+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				
5									



Figure 2. Experimental values (•) and correlation curves for $H_m^{\rm E}$ vs x_1 at 299.15 K for the binary mixtures $C_{u-1}H_{2u-1}COOC_2H_5$ (1) + CH₃(CH₃)C(OH)CH₃ (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 (\bigcirc).

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^{o} , for
tert-Buta	nol			-

ieri-Dula	1101				
ТK	p_i^0/kPa	ТK	p_i^0/kPa	ТK	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) (\triangle , \Box) 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	Α	В	С	$s(p_i^0)^c/kPa$	Δ <i>T</i> /K	references
<i>tert</i> -butanol	6.600 44 6.356 48 6.328 30	1238.69 1107.06 1092.97	85.99 101.05 102.65	0.09	330 - 370 330 - 365	this work Riddick et al. (ref 10) Boublik et al. (ref 15)
ethyl methanoate ethyl ethanoate ethyl propanoate ethyl butanoate	$\begin{array}{c} 6.650\ 74\\ 6.596\ 55\\ 6.301\ 80\\ 6.363\ 64 \end{array}$	1431.31 1480.71 1382.89 1496.03	19.09 27.61 50.09 50.90		300-350 300-370 340-390 370-410	Soto et al. (ref 3) Hernández et al. (ref 14) Hernández et al. (ref 14) 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	а	b	С	ω	references
<i>tert</i> -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)

 $a^{a}\log(p_{i}^{0}/k\text{Pa}) = A - B/(T/(K) - C)$. $b\log(p_{i,r}^{0}) = a - b/(T_{r} - c)$. ^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) + CH₃(CH₃)C(OH)CH₃ (2). Considering that the vapor phase was not ideal, the activity coefficients for the components in the liquid phase were calculated by

$$\ln \gamma_{i} = \ln \left(\frac{py_{i}}{p_{i}^{0}x_{i}} \right) + \frac{(B_{ii} - V_{i}^{0})(p - p_{i}^{0})}{RT} + \frac{p}{RT} \sum_{k} \sum_{k} y_{j}y_{k}(2\delta_{ji} - \delta_{jk})$$
(3)

where

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

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 Danner¹⁸ 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 $G_{\rm m}^{\rm E}/RT$, 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 $\bar{\delta} = \sum_{i} (y_{i, exp} - z_{i})$ $y_{i,cal}$ / $N \le 0.01$. 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



Figure 4. Representation of experimental VLE values (**●**) and correlation curves for T vs x_1 , y_1 for the binary mixtures $C_{u-1}H_{2u-1}$ -COOC₂H₅ (1) + CH₃(CH₃)C(OH)CH₃ (2); labels indicate the u values. Dashed lines indicate curves estimated using the UNIFAC model (ref 5).

 $(d T/dx)_p = 0$, 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 $p_{i,r}^0$ versus $1/T_r$ 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

$ \begin{array}{c} \mbox{Tr} 0 \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	<i>T</i> /K	<i>X</i> 1	y_1	γ_1	γ_2	$G_{\rm m}^{\rm E}/RT$	<i>T</i> /K	<i>X</i> 1	y_1	γ_1	γ_2	$G_{\rm m}^{\rm E}/RT$	<i>T</i> /K	<i>X</i> 1	y_1	γ_1	γ_2	$G_{\rm m}^{\rm E}/RT$
$ \begin{array}{c} 334.13 & 0.0197 & 0.0712 & 1.006 & 1.001 & 0.010 & 342.4 & 0.243 & 0.5452 & 1.391 & 1.012 & 0.089 & 333.85 & 0.6684 & 0.8395 & 1.083 & 1.285 & 0.137 \\ 351.69 & 0.0559 & 0.1837 & 1.562 & 1.003 & 0.027 & 340.71 & 0.288 & 0.5664 & 1.348 & 1.026 & 0.165 & 331.45 & 0.6664 & 0.8395 & 1.083 & 1.285 & 0.137 \\ 359.03 & 0.0694 & 0.2210 & 1.542 & 0.098 & 0.040 & 339.95 & 0.3116 & 0.6164 & 1.322 & 1.034 & 0.113 & 325.60 & 0.8995 & 0.8482 & 1.048 & 1.388 & 0.110 \\ 349.21 & 0.0898 & 0.2961 & 1.525 & 0.998 & 0.040 & 339.95 & 0.314 & 0.127 & 1.075 & 0.852 & 0.8025 & 0.9444 & 1.043 & 1.478 & 0.079 \\ 347.77 & 0.1245 & 0.333 & 1.505 & 1.000 & 0.060 & 335.65 & 0.341 & 0.144 & 0.118 & 322.82 & 0.824 & 0.497 & 1.487 & 0.079 \\ 345.80 & 0.113 & 0.426 & 0.422 & 1.052 & 1.005 & 0.356 & 0.7414 & 0.718 & 1.225 & 1.07 & 0.141 & 327.74 & 0.584 & 0.973 & 1.005 & 1.664 & 0.027 \\ 344.40 & 0.136 & 0.422 & 1.425 & 1.005 & 0.073 & 334.69 & 0.7391 & 1.126 & 1.130 & 0.143 & 327.74 & 0.584 & 0.973 & 1.000 & 1.662 & 0.063 \\ 344.00 & 0.136 & 0.522 & 1.467 & 1.069 & 0.047 & 334.49 & 0.336 & 0.7770 & 1.170 & 1.130 & 0.144 \\ 35.16 & 0.0236 & 0.5224 & 1.071 & 1.096 & 0.047 & 334.59 & 0.3386 & 0.7770 & 1.160 & 1.163 & 0.145 \\ \hline \\ \hline \\ 55.18 & 0.0234 & 0.0558 & 1.313 & 1.002 & 0.003 & 352.27 & 0.2390 & 0.386 & 1.211 & 1.018 & 0.054 & 350.14 & 0.5619 & 0.6104 & 1.087 & 1.096 & 0.874 \\ 35.42 & 0.044 & 0.057 & 1.313 & 1.002 & 0.003 & 352.27 & 0.2390 & 0.3381 & 1.057 & 1.138 & 1.048 & 0.774 & 0.4868 & 0.774 & 1.143 & 0.084 \\ 34.42 & 0.041 & 0.167 & 1.228 & 1.002 & 0.023 & 351.48 & 0.0380 & 0.371 & 1.138 & 1.044 & 0.057 & 344.81 & 0.6629 & 0.613 & 1.474 & 0.714 \\ 35.42 & 0.047 & 0.137 & 0.072 & 34.48 & 0.062 & 0.338 & 0.411 & 1.074 & 0.073 & 34.68 & 0.774 & 0.718 & 1.274 & 0.054 \\ 35.43 & 0.0464 & 0.124 & 1.040 & 0.023 & 351.68 & 0.3390 & 0.431 & 1.177 & 0.705 & 34.84 & 0.068 & 0.8724 & 0.716 & 1.142 & 0.064 \\ 35.44 & 0.0468 & 0.2424 & 1.041 & 0.052 & 0.5351 & 1.071 & 1.075 & 0.874 & 0.788 & 80.301 & 0.775 & 0.974 & 0.788 & 80.774 & 0.788 & 80.610 & 0.778$							Ethy	yl Metha	noate (1)	+ tert	Butano	l (2)						
352.79 0.0380 0.1361 1.584 1.004 0.022 341.62 0.2687 1.546 1.003 0.277 0.2825 0.0779 0.8825 1.071 0.310 0.330 0.0130 0.329 0.389 0.310 0.300 0.310 0.300 0.310 0.300 0.310 0.300 0.3114 0.7149 0.8255 0.0779 0.8842 1.048 1.038 0.013 0.3116 0.6194 1.031 1.040 0.07579 0.8842 1.041 1.538 0.014 1.314 1.040 0.07579 0.8842 1.042 1.464 0.073 3.011 0.3102 0.0769 0.314 0.7144 1.228 1.087 0.163 0.226 0.9411 1.011 1.538 0.041 34.63 0.1240 1.427 1.446 1.003 0.083 3.547 0.555 1.177 1.143 0.141 327.44 0.9808 0.9933 1.000 1.662 0.067 3.547 0.568 0.339 1.041 1.051 1.618 0.447 1.446 1.037 1.641 1.27 0.779	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
$ \begin{array}{c} 351.6 0 \ 0.0550 \ 0.1837 \ 1.562 \ 1.003 \ 0.027 \ 340.7 \ 0.288 \ 0.5944 \ 1.348 \ 1.026 \ 0.150 \ 331.6 \ 0.0841 \ 0.084 \ 0.388 \ 0.130 \ 339.5 \ 0.316 \ 0.6194 \ 0.328 \ 0.384 \ 0.131 \ 339.5 \ 0.370 \ 0.6761 \ 0.322 \ 1.034 \ 0.118 \ 329.8 \ 0.310 \ 0.330 \ 5.0 \ 0.330 \ 5.0 \ 0.330 \ 5.0 \ 0.330 \ 5.0 \ 0.330 \ 5.0 \ 0.330 \ 5.0 \ 0.330 \ 5.0 \ 0.330 \ 5.0 \ 0.330 \ 5.0 \ 0.330 \ 5.0 \ 0.330 \ 5.0 \ 0.330 \ 5.0 \ 0.330 \ 5.0 \ 0.330 \ 5.0 \ 0.330 \ 5.0 \ 5.0 \ 0.330 \ 5.0 $	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
350.93 0.0694 0.2210 1.546 1.000 0.030 339.02 0.309 0.2409 0.6406 1.322 1.011 320.82 0.044 1.341 1.416 0.095 348.40 0.1136 0.3301 1.516 0.997 0.044 1.341 1.238 0.0464 0.241 1.242 1.047 1.143 1.228 1.087 0.142 1.442 1.041 1.538 0.041 1.341 0.373 0.340 0.252 0.9216 0.9411 1.010 1.568 0.444 1.041 1.538 0.143 3.141 0.7143 1.228 1.087 1.045 1.040 1.051 1.040 1.043 3.274 0.568 0.941 1.041 1.538 0.100 1.043 1.044 1.023 1.041 <td>351.69</td> <td>0.0559</td> <td>0.1837</td> <td>1.562</td> <td>1.003</td> <td>0.027</td> <td>340.71</td> <td>0.2889</td> <td>0.5964</td> <td>1.348</td> <td>1.026</td> <td>0.105</td> <td>331.45</td> <td>0.6941</td> <td>0.8525</td> <td>1.070</td> <td>1.310</td> <td>0.130</td>	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
$\begin{array}{c} 349.2 & 0.0980 & 0.2961 & 1.52 & 0.998 & 0.040 & 330.2 & 0.3409 & 0.6460 & 1.302 & 1.044 & 0.118 & 329.3 & 0.802 & 0.9044 & 1.034 & 1.416 & 0.095 \\ 347.77 & 0.1245 & 0.350 & 1.505 & 1.000 & 0.051 & 337.30 & 0.025 & 0.6939 & 1.247 & 1.072 & 0.131 & 328.2 & 0.896 & 0.9844 & 0.9246 & 0.9246 & 0.9241 & 0.101 & 1.588 & 0.044 \\ 345.8 & 0.172 & 0.4427 & 1.464 & 1.003 & 0.068 & 338.5 & 0.4590 & 0.7318 & 1.228 & 1.087 & 0.138 & 328.2 & 0.9216 & 0.6611 & 1.01 & 1.588 & 0.044 \\ 345.8 & 0.172 & 0.4427 & 1.464 & 1.003 & 0.068 & 338.5 & 0.4590 & 0.7318 & 1.278 & 1.107 & 0.143 & 327.44 & 0.9868 & 0.9933 & 1.000 & 1.664 & 0.207 \\ 344.40 & 0.184 & 0.4262 & 1.452 & 1.006 & 0.077 & 33.5.0 & 1.0990 & 0.7553 & 1.178 & 1.130 & 0.143 & 327.44 & 0.9868 & 0.9933 & 1.000 & 1.662 & 0.006 \\ 344.0 & 0.2037 & 0.4907 & 1.425 & 1.006 & 0.077 & 33.5.0 & 1.0990 & 0.7553 & 1.150 & 1.163 & 0.143 & 327.44 & 0.9868 & 0.9933 & 1.000 & 1.662 & 0.006 \\ 343.0 & 0.258 & 0.5224 & 1.027 & 1.009 & 0.084 & 33.41 & 0.593 & 34.941 & 0.561 & 9.6104 & 1.087 & 1.096 & 0.87 \\ 355.18 & 0.0234 & 0.0588 & 1.310 & 1.001 & 0.010 & 352.27 & 0.2368 & 0.3066 & 1.211 & 1.018 & 0.053 & 349.81 & 0.6629 & 0.6913 & 1.054 & 1.143 & 0.080 \\ 354.7 & 0.0666 & 0.1012 & 1.289 & 1.002 & 0.013 & 352.27 & 0.2883 & 0.3871 & 1.193 & 1.024 & 0.067 & 34.980 & 0.6478 & 1.068 & 1.120 & 0.087 \\ 353.41 & 0.047 & 0.1367 & 1.275 & 1.004 & 0.027 & 351.84 & 0.3363 & 0.491 & 1.172 & 1.032 & 0.076 & 34.980 & 0.8102 & 0.8129 & 1.027 & 1.214 & 0.055 \\ 353.84 & 0.137 & 0.169 & 0.328 & 0.1338 & 0.4091 & 1.172 & 1.032 & 0.076 & 34.950 & 0.848 & 0.8415 & 1.061 & 1.270 & 0.051 \\ 353.41 & 0.167 & 0.198 & 1.237 & 0.108 & 351.36 & 0.3281 & 1.104 & 1.068 & 0.3645 & 1.091 & 1.076 & 0.088 \\ 353.41 & 0.167 & 0.108 & 0.351 & 0.052 & 5.351 & 1.101 & 1.161 & 0.108 & 363.60 & 0.7285 & 0.5811 & 1.043 & 1.163 & 0.065 \\ 353.40 & 0.0458 & 0.0271 & 1.231 & 1.012 & 0.049 & 350.40 & 0.573 & 0.361 & 0.073 & 36.10 & 0.773 & 0.8910 & 0.721 & 1.014 & 1.056 & 36.049 & 0.087 & 35.360 & 0.778 & 0.871 & 0.071 & 35.60 & 0.07$	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
348.40 0.1136 0.391 1.66 0.997 0.044 338.18 0.3704 0.6702 1.276 1.025 0.124 322.3 0.8464 0.0246 1.023 1.178 0.079 346.30 0.1528 0.4907 1.485 1.000 0.663 353.50 0.4925 1.464 1.005 1.668 0.444 344.80 0.1426 1.462 1.005 1.668 0.444 1.468 1.005 1.668 0.444 343.10 0.2256 0.5224 1.007 1.033 1.178 1.130 0.143 327.78 0.5844 0.9733 1.000 1.666 0.006 353.01 0.2256 0.5224 1.007 1.009 0.877 1.151 1.163 0.144 350.14 0.6104 1.087 1.096 0.607 354.00 0.0447 0.6071 1.299 1.002 0.013 352.77 0.2130 1.224 1.021 0.6673 349.60 0.6473 1.648 1.430 0.648 354.0 0.0447 0.6671 1.299 1.002 <t< td=""><td>349.21</td><td>0.0989</td><td>0.2961</td><td>1.525</td><td>0.998</td><td>0.040</td><td>339.02</td><td>0.3409</td><td>0.6460</td><td>1.302</td><td>1.044</td><td>0.118</td><td>329.85</td><td>0.8025</td><td>0.9044</td><td>1.034</td><td>1.416</td><td>0.095</td></t<>	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
347.7 0.1245 0.131 328.20 0.981 0.9443 1.014 1.338 0.0081 346.30 0.152 0.4927 1.464 1.000 0.068 338.57 0.4599 0.7318 1.225 1.107 0.143 327.44 0.9844 0.9773 1.005 1.664 0.027 344.48 0.143 0.422 1.225 1.007 0.143 327.44 0.9864 0.9773 1.005 1.664 0.007 341.40 0.2258 0.5224 1.407 1.009 0.843 334.10 0.2268 0.524 1.001 1.562 0.2034 0.358 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 1.006 0.097 355.16 0.0234 0.058 1.313 1.206 1.1018 0.054 361.0 0.561 1.017 1.014 1.048 0.086 354.0 0.142 1.29 1.002 0.103 352.77 0.2189 0.3333 1.04171 1.010	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
346.30 0.1528 0.4097 1.485 1.000 0.666 335.87 0.4590 7.181 1.205 1.07 0.141 327.44 0.9540 0.9731 1.000 1.662 0.006 344.80 0.1262 0.4267 1.452 1.000 0.6755 1.178 1.130 0.141 327.44 0.9868 0.9933 1.000 1.662 0.006 344.40 0.2258 0.5224 1.407 1.009 0.044 34.19 0.5396 0.7710 1.150 1.138 0.144 353.16 0.0224 0.0358 1.011 1.0101 0.010 352.27 0.2369 0.368 1.211 1.018 0.593 4.997 0.6989 0.6478 1.087 1.000 0.643 354.0 0.0447 0.0667 1.257 1.004 0.027 351.84 0.2389 0.339 1.44 1.027 0.074 340.68 0.779 1.027 1.14 0.058 3.538 0.128 1.225 1.007 0.352 0.775 1.021 1.004 1.035 0.491 1.011 <t< td=""><td>347.77</td><td>0.1245</td><td>0.3530</td><td>1.505</td><td>1.000</td><td>0.051</td><td>337.30</td><td>0.4025</td><td>0.6939</td><td>1.249</td><td>1.072</td><td>0.131</td><td>328.66</td><td>0.8880</td><td>0.9443</td><td>1.014</td><td>1.538</td><td>0.061</td></t<>	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
343.8 0.1720 0.4427 1.464 1.003 0.068 335.87 0.4390 0.7515 1.178 1.103 0.143 327.78 0.9963 0.9933 1.000 1.662 0.006 344.40 0.143 0.425 1.000 0.0490 0.755 1.178 1.130 0.143 327.78 0.9963 0.9933 1.000 1.662 0.006 341.0 0.2258 0.5224 1.007 0.039 325.77 0.5396 0.7710 1.130 1.614 0.045 35.18 0.0384 0.5619 0.6104 1.087 1.096 0.087 355.18 0.0344 0.0584 1.311 1.001 0.010 352.52 0.2380 0.3861 1.201 0.063 349.97 0.6629 0.6104 1.087 1.430 0.082 354.57 0.0686 0.112 1.259 1.002 0.023 351.46 0.3633 0.3821 1.184 1.027 0.073 346.60 0.6120 8.122 1.021 1.214 0.053 33.10 1.313 0.227 1.221 1.012	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
344.00 0.1643 0.1642 1.000 1.0490 0.735 1.170 1.138 0.144 344.00 0.2258 0.5224 1.007 0.334.79 0.5095 0.7711 1.150 1.148 0.144 343.10 0.2258 0.5224 1.407 1.009 0.004 344.19 0.5395 0.711 1.150 0.143 0.614 1.087 1.006 0.007 355.16 0.0334 0.0581 1.313 1.002 0.009 352.77 0.2139 0.2386 1.211 1.168 0.059 349.97 0.6098 0.6144 1.087 1.096 0.087 354.6 0.0447 0.0671 1.299 1.002 0.013 352.27 0.2399 0.3339 1.204 1.021 0.063 349.81 0.6629 0.6913 1.054 1.143 0.083 354.2 0.0447 0.1367 1.275 1.040 0.052 3.534 0.614 0.681 0.629 0.6913 1.054 1.140 0.653 353.4 0.1648 0.5281 0.3033 0.6261	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
344.94 0.2037 0.4907 1.423 1.000 0.077 334.79 0.5396 0.777 1.150 1.163 0.144 343.10 0.2286 0.5224 1.027 1.000 0.007 332.77 0.130 1.163 0.145 Ethyl Ethamaette(1) + tert-Butanol (2) 355.06 0.0334 0.0508 1.310 1.001 0.010 352.57 0.2380 0.3281 1.212 1.018 0.059 349.97 0.6098 0.6478 1.068 1.143 0.080 354.50 0.0486 0.1012 1.289 1.002 0.033 352.27 0.2590 0.3331 1.012 0.007 349.81 0.6629 0.9131 1.174 1.174 1.138 1.142 0.063 349.81 0.6612 0.8012 0.211 1.11 0.112 1.008 0.86 0.8102 0.8174 0.183 0.141 1.145 0.080 0.8174 0.318 0.3339 0.141 1.145 0.081 0.8129 1.214 0.063 333.41 0.157 0.817 0.217 0.381	344.80	0.1843	0.4626	1.452	1.005	0.073	335.01	0.4990	0.7555	1.170	1.130	0.143	327.44	0.9868	0.9933	1.000	1.662	0.006
$ \begin{array}{c} 533.10 & 0.2258 & 0.524 & 1.40' & 1.09' & 0.09' & 1.34' & 1.00' & 1.09' & 0.09' & 1.34' & 0.539 & 0.770' & 1.130' & 1.168' & 0.133' \\ $	344.04	0.2037	0.4907	1.425	1.006	0.077	334.79	0.5095	0.7611	1.170	1.138	0.144						
Ethyl Ethanoate (1) + tert-Butanol (2) S55.18 0.003 355.18 0.013 357.02 357.07 0.110 0.013 357.02 0.013 357.02 0.013 357.02 0.013 357.02 0.013 357.02 0.013 357.02 0.013 357.02 0.013 357.02 0.027 357.01 0.027 357.01 0.027 357.01 0.077 349.63 0.8129 0.771 1.214 0.072 357.01 0.073 349.59 0.8129 0.212 1.214 0.072 357.01 0.073 349.59 0.8428 0.8428 0.8428 0.8428 0.8428 0.8428 0.851 1.214 0.001 357.57	343.10	0.2238	0.3224	1.407	1.009	0.084	334.19	0.5396	0.7770	1.150	1.103	0.145						
333.18 0.023 1.313 1.002 0.009 332.17 0.2139 0.2834 1.223 1.014 0.034 330.97 0.0508 0.211 1.018 0.0547 0.0663 349.81 0.0628 0.6478 1.068 1.024 0.063 349.81 0.6628 0.6478 1.068 1.121 0.084 354.57 0.0568 0.111 2.295 1.003 0.020 352.05 0.2823 0.557 1.184 1.024 0.063 349.81 0.7679 0.7759 1.027 1.214 0.055 353.85 0.1235 0.142 2.591 1.005 0.032 351.60 0.3391 0.4701 1.145 1.047 0.0878 349.59 0.8428 0.8415 1.016 1.270 0.051 353.40 0.1668 0.2281 1.221 1.010 0.042 355.08 0.4771 0.5384 1.114 1.069 0.8428 0.8415 1.016 1.270 0.051 353.40 0.668 0.2281 1.221 1.010 0.044 350.41 0.557 0.571 0.771 <td>955 10</td> <td>0.0004</td> <td>0.0250</td> <td>1 9 1 9</td> <td>1 009</td> <td>0.000</td> <td>Eth</td> <td>yl Ethai</td> <td>10ate (1)</td> <td>+ tert-</td> <td>Butanol</td> <td>(2)</td> <td>950 14</td> <td>0 5010</td> <td>0.0104</td> <td>1 007</td> <td>1 000</td> <td>0.007</td>	955 10	0.0004	0.0250	1 9 1 9	1 009	0.000	Eth	yl Ethai	10ate (1)	+ tert-	Butanol	(2)	950 14	0 5010	0.0104	1 007	1 000	0.007
335.00 0.033 0.0308 1.310 1.001 0.011 352.2 0.2309 0.3086 1.211 1.103 0.0093 319.97 0.0098 0.0098 1.0098 1.100 1.100 0.013 352.27 0.2590 0.333 1.204 1.021 0.063 319.97 0.0098 0.0217 315.40 0.047 318.41 1.141 1.021 0.063 319.97 0.0778 0.0773 1.024 0.073 319.97 0.0783 340.60 0.7797 0.7759 1.211 0.0053 333.92 0.181 1.141 1.027 0.0773 340.60 0.8102 0.8121 1.141 1.025 0.0773 349.50 0.4242 0.0161 1.141 1.027 0.073 349.50 0.4242 0.016 1.141 0.050 0.773 0.271 1.141 0.068 349.70 0.4848 0.8322 0.071 1.340 0.042 353.04 0.168 0.837 0.141 0.051 0.351 0.071 350.41 0.551 1.017 1.075 0.863 0.4848 0.322 0.0922 0.0051 <	333.18	0.0234	0.0338	1.313	1.002	0.009	332.11	0.2139	0.2834	1.223	1.014	0.054	330.14	0.3019	0.0104	1.087	1.090	0.087
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	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	0.64/8	1.068	1.120	0.084
334.3 0.0080 0.0102 1.228 0.002 0.020 0.220.3 0.321 1.143 1.006 349.63 0.744 0.7416 1.039 1.171 0.074 333.8 0.1235 0.1742 1.255 0.007 331.8 0.181 1.114 1.015 1.027 1.214 0.068 333.8 0.1217 2.250 1.008 0.038 31.66 0.3329 0.4361 1.151 1.047 0.848 0.848 0.8112 1.021 1.021 0.051 333.8 0.1573 0.2161 1.243 1.010 0.042 351.86 0.355 0.355 0.055 1.105 0.085 349.88 0.8322 0.9252 1.001 1.374 0.022 353.08 0.157 0.261 0.218 1.377 0.996 0.004 350.80 1.057 0.085 349.88 0.843 0.9322 0.9252 1.001 1.374 0.022 355.80 0.0261 0.0218 1.377 0.996 0.001 350.40 0.5111 0.381 1.114 1.069 0.	354.90	0.0447	0.06/1	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
$\begin{array}{c} 334.2 & 0.0947 & 0.1367 & 1.275 & 1.004 & 0.027 & 331.84 & 0.3063 & 0.3821 & 1.184 & 1.027 & 0.070 & 349.63 & 0.612 & 0.8122 & 0.127 & 1.214 & 0.063 \\ 353.84 & 0.1417 & 0.1969 & 1.250 & 1.008 & 0.032 & 351.60 & 0.330 & 0.4091 & 1.172 & 1.032 & 0.074 & 349.60 & 0.812 & 0.812 & 0.121 & 1.016 & 1.270 & 0.051 \\ 353.41 & 0.1573 & 0.2161 & 1.243 & 1.010 & 0.042 & 351.08 & 0.3901 & 0.4701 & 1.145 & 1.047 & 0.085 & 349.48 & 0.8415 & 1.016 & 1.270 & 0.023 \\ 353.00 & 0.1668 & 0.2281 & 1.242 & 1.010 & 0.044 & 350.81 & 0.4386 & 0.5056 & 1.130 & 1.057 & 0.085 & 349.88 & 0.322 & 0.9252 & 1.001 & 1.374 & 0.022 \\ 353.00 & 0.2602 & 0.2622 & 1.221 & 1.013 & 0.052 & 350.471 & 0.5384 & 1.114 & 1.069 & 0.086 & 363.10 & 0.9778 & 0.974 & 0.998 & 1.424 & 0.066 \\ 352.91 & 0.2009 & 0.2682 & 1.227 & 1.013 & 0.052 & 350.471 & 0.5384 & 1.114 & 1.069 & 0.086 & 363.10 & 0.9778 & 0.571 & 0.374 & 0.998 & 1.424 & 0.065 \\ 355.88 & 0.0458 & 0.0378 & 1.357 & 0.997 & 0.011 & 350.94 & 0.5141 & 0.3871 & 1.097 & 1.086 & 0.087 & 365.38 & 0.5811 & 1.034 & 1.163 & 0.065 \\ 355.88 & 0.0458 & 0.0378 & 1.357 & 0.997 & 0.011 & 350.94 & 0.5141 & 0.3871 & 1.097 & 1.086 & 0.087 & 365.38 & 0.8115 & 0.6790 & 1.019 & 1.197 & 0.054 \\ 356.80 & 0.1485 & 1.377 & 0.996 & 0.013 & 360.01 & 0.5421 & 0.491 & 1.086 & 1.089 & 0.088 & 365.24 & 0.8056 & 0.6711 & 1.019 & 1.197 & 0.049 \\ 366.80 & 0.1485 & 1.277 & 1.007 & 0.051 & 360.49 & 0.5739 & 0.4357 & 1.076 & 1.100 & 0.086 & 365.19 & 0.816 & 0.755 & 1.017 & 1.207 & 0.455 \\ 356.80 & 0.2879 & 0.1786 & 1.247 & 1.013 & 0.069 & 360.97 & 0.6033 & 0.4604 & 1.066 & 1.116 & 0.082 & 367.73 & 0.810 & 0.7921 & 1.008 & 1.260 & 0.377 & 366.9 & 0.800 & 0.755 & 1.017 & 1.216 & 0.037 \\ 356.89 & 0.279 & 0.1786 & 1.427 & 0.13 & 0.069 & 360.97 & 0.6133 & 0.4604 & 1.066 & 1.116 & 0.082 & 367.73 & 0.8810 & 0.755 & 1.017 & 1.216 & 0.037 \\ 357.9 & 0.352 & 0.2710 & 1.270 & 0.043 & 365.97 & 0.5121 & 0.104 & 1.183 & 0.076 & 371.05 & 0.972 & 0.9860 & 0.5739 & 1.018 & 1.380 & 0.565 \\ 356.38 & 0.4655 & 0.3242 & 1.407 & 1.052 & 0.863 & 0.5160 & 0.25$	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	1.1//	0.072
333.88 0.123 0.1742 1.239 0.1742 1.239 0.0742 1.241 0.0321 1.241 0.033 0.0333 0.1031 0.0325 0.3136 0.1325 0.0342 0.8412 0.8412 0.0412 1.121 0.034 353.41 0.1573 0.2161 1.243 1.010 0.044 351.08 0.380 0.166 0.5281 1.010 0.044 350.80 0.380 0.166 0.5281 1.037 0.022 2.001 1.374 0.022 353.80 0.1687 0.2621 1.231 1.012 0.049 350.80 0.471 0.5384 1.114 1.069 0.086 350.10 0.9778 0.9744 0.998 1.424 0.006 355.80 0.0261 0.0218 1.377 0.997 0.011 359.64 0.5411 0.3871 1.097 1.086 0.088 364.11 0.7285 0.5811 1.034 1.163 0.065 355.80 0.784 0.6811 1.010 0.83 359.61 0.786 0.8363 0.101 0.7285 0.5811 1.019 1.17	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
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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
333.4 0.1673 0.2161 1.243 1.010 0.042 351.08 0.3991 0.4701 1.145 1.047 0.082 349.74 0.8878 0.8878 0.8878 0.1877 0.2321 1.010 0.044 350.81 0.386 0.5055 1.130 1.057 0.085 349.74 0.8878 0.8878 0.9222 1.011 0.042 350.81 0.386 0.5055 1.107 1.075 0.885 350.10 0.9778 0.9744 0.988 1.424 0.006 355.98 0.0261 0.0218 1.377 0.996 0.000 359.73 0.5212 0.3924 1.094 1.086 0.888 363.41 0.7282 0.8264 0.8648 0.878 0.8451 1.091 1.086 0.888 364.11 0.7462 0.6201 1.19 1.195 0.050 355.86 0.4231 1.091 1.086 0.888 365.42 0.8506 0.811 1.019 1.09 1.086 0.883 365.41 0.476 1.017 0.423 1.014 0.383 0.417 1.014 0.386 0.6563 366	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
333.30 0.1668 0.2281 1.242 1.010 0.044 350.81 0.4386 0.5056 1.1057 0.085 351.00 0.9778 0.9784 0.998 1.424 0.006 352.91 0.2009 0.2682 1.227 1.013 0.052 350.88 1.107 1.075 0.087 361.10 0.9778 0.9744 0.998 1.424 0.066 355.80 0.0261 0.0218 1.377 0.997 0.011 350.41 0.5052 0.5635 1.107 1.075 0.087 363.36 0.7285 0.5811 1.034 1.163 0.065 355.80 0.0261 0.0218 1.537 0.997 0.011 359.73 0.5212 0.3926 1.097 1.086 0.088 364.11 0.762 0.6201 1.019 1.197 0.493 356.80 0.1485 0.1485 0.1481 0.001 350.73 0.5212 0.3926 1.091 1.086 0.088 365.91 0.3816 0.7555 1.017 1.207 0.453 356.63 0.1485 0.1485 0.57	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
333.08 0.1857 0.2501 1.221 1.012 0.049 350.58 0.4771 0.5384 1.117 1.065 0.087 352.91 0.2009 0.2682 1.227 1.013 0.052 350.41 0.5635 1.107 1.075 0.087 355.80 0.0218 1.037 0.996 0.005 359.41 0.3635 1.097 1.086 0.088 363.36 0.7285 0.5811 1.034 1.63 0.065 355.96 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 1.049 356.43 0.147 1.344 1.002 0.033 360.28 0.5539 1.0437 1.066 0.087 365.34 0.816 0.7655 1.017 1.027 0.453 356.63 0.1865 0.1485 1.277 1.007 0.051 360.91 0.6005 4.573 1.066 1.117 0.085 366.79 0.8000 0.7456 1.012 1.216 0.037	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
332.91 0.2009 0.2682 1.227 1.013 0.052 350.41 0.5052 0.5635 1.107 1.075 0.087 355.80 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 0.065 355.80 0.0784 0.0641 1.341 1.001 0.024 359.73 0.5212 0.3926 1.094 1.086 0.088 365.34 0.815 0.6701 1.019 1.076 0.088 365.34 0.815 0.6701 1.019 1.09 1.091 1.095 0.050 365.38 0.1423 0.1147 1.304 1.002 0.393 360.28 0.5598 0.4239 1.081 1.101 0.086 365.91 0.8316 0.7055 1.017 1.027 0.045 356.89 0.1423 0.118 1.007 0.573 0.6613 1.117 0.082 366.79 0.8900 0.752 1.001 1.024 0.074 361.39 0.6289 0.452 1.056 </td <td>353.08</td> <td>0.1857</td> <td>0.2501</td> <td>1.231</td> <td>1.012</td> <td>0.049</td> <td>350.58</td> <td>0.4771</td> <td>0.5384</td> <td>1.114</td> <td>1.069</td> <td>0.086</td> <td>350.10</td> <td>0.9778</td> <td>0.9744</td> <td>0.998</td> <td>1.424</td> <td>0.006</td>	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
Ethyl Propanolet (1) + tert-Butanol (2) 355.80 0.0218 0.0218 1.377 0.996 0.005 359.27 0.4845 0.3645 1.109 1.068 0.088 363.10 0.7285 0.5811 1.013 1.163 0.061 355.80 0.0478 0.0611 1.341 1.001 0.024 359.73 0.5212 0.3926 1.094 1.089 0.088 364.11 0.7628 0.6201 1.029 1.101 0.061 356.38 0.1427 1.034 1.000 0.031 360.10 0.5421 0.4911 1.086 1.087 365.24 0.8010 0.7155 1.017 1.027 0.045 356.38 0.1485 1.277 1.007 0.603 360.97 0.6033 0.4604 1.066 1.116 0.085 368.79 0.8010 0.7455 1.012 1.216 0.037 357.37 0.2717 1.210 1.117 0.620 369.91 0.522 0.8940 0.522 0.8940 0.5	352.91	0.2009	0.2682	1.227	1.013	0.052	350.41	0.5052	0.5635	1.107	1.075	0.087						
355.80 0.0261 0.0218 1.377 0.996 0.005 359.27 0.4845 0.3845 1.098 1.008 363.36 0.7285 0.5811 1.0.34 1.63 0.061 355.88 0.0458 0.0378 1.337 0.997 0.011 359.64 0.5141 0.3871 1.097 1.086 0.088 364.11 0.7628 0.6200 1.029 1.107 0.040 355.96 0.0744 0.0641 1.341 1.000 0.021 360.01 0.5421 0.4991 1.086 1.086 1.087 365.38 0.8115 0.6705 1.017 1.027 0.045 356.63 0.1485 1.147 1.013 0.060 360.91 0.6005 0.4573 1.066 1.116 0.082 367.73 0.8910 0.7445 1.021 1.021 1.021 1.021 1.021 1.021 1.021 1.021 1.021 1.021 1.021 0.025 357.75 0.3252 0.2217 1.191 1.024 361.96 0.6297 0.5121 1.049 1.188 0.076 371.05 0.979							Eth	yl Propa	noate (1)	+ tert-	Butano	l (2)						
355.88 0.0458 0.0458 0.0458 0.0458 0.0641 1.337 0.997 0.011 359.64 0.5141 0.3871 0.0271 0.088 366.11 0.7628 0.6201 1.019 1.086 0.088 366.11 0.7628 0.6711 1.019 1.176 0.050 356.49 0.1102 0.0896 1.323 1.000 0.031 360.01 0.5421 0.4991 1.086 0.087 365.24 0.8060 0.7615 1.017 1.027 0.045 356.68 0.1485 0.1477 1.007 0.051 360.49 0.5739 0.4357 1.066 1.116 0.082 366.79 0.8000 0.7456 1.012 1.216 0.031 356.89 0.2791 1.786 1.247 1.013 0.069 360.97 0.6133 0.4604 1.066 1.116 0.082 366.79 0.8000 0.791 1.024 0.031 36.049 0.6597 0.5112 1.049 1.38 0.076 371.05 0.979 0.9552 1.002 1.264 0.014 355.99 0.221 0	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
355.96 0.0784 0.0641 1.341 1.001 0.024 356.12 0.3926 0.088 365.24 0.8050 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 0.6705 1.017 1.207 0.049 356.38 0.1425 0.1485 1.277 1.007 0.051 360.49 0.5739 0.4357 1.066 1.117 0.086 365.79 0.8600 0.7456 1.012 1.216 0.037 357.31 0.2791 0.1786 1.247 1.013 0.060 360.97 0.6033 0.4604 1.066 1.116 0.082 368.72 0.9220 0.8441 1.008 1.208 0.373 0.522 0.9211 1.008 1.264 0.011 357.30 0.352 0.2717 1.171 1.043 0.628 365.39 1.043 1.449 0.738 0.8600 0.5739 1.002 1.264 0.017 356.48 0.4088 0.	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
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 0.049 356.63 0.1423 0.1147 1.304 1.002 0.039 360.28 0.5598 0.4235 1.076 1.106 0.086 366.79 0.8600 0.7456 1.012 1.207 0.045 356.63 0.279 0.1786 1.247 1.013 0.060 360.91 0.6005 0.4573 1.066 1.117 0.082 366.79 0.8600 0.7456 1.012 1.008 1.216 0.037 357.75 0.3259 0.2517 1.195 1.024 0.074 361.96 0.6289 0.4832 1.059 1.184 0.072 388.46 0.4088 0.3082 1.140 1.052 0.844 362.51 0.6885 0.5394 1.043 1.149 0.072 385.46 0.4088 0.3024 1.411 1.069 0.873 366.28 0.512 1.041 1.131 1.081 0.075 1.080	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
356.38 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 0.0437 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 0.060 360.97 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 0.074 361.96 0.6597 0.512 1.049 1.138 0.076 371.05 0.9797 0.9552 1.002 1.280 0.007 358.46 0.4088 0.3424 1.117 1.069 0.87 362.93 0.7081 0.552 1.037 1.156 0.068 1.002 1.280 0.007 355.39 0.0214 1.472 0.996 </td <td>356.19</td> <td>0.1102</td> <td>0.0896</td> <td>1.323</td> <td>1.000</td> <td>0.031</td> <td>360.01</td> <td>0.5421</td> <td>0.4091</td> <td>1.086</td> <td>1.096</td> <td>0.087</td> <td>365.38</td> <td>0.8115</td> <td>0.6790</td> <td>1.019</td> <td>1.197</td> <td>0.049</td>	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
356.63 0.1865 0.1485 1.247 1.007 0.051 360.49 0.5739 0.4357 1.016 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 0.082 366.79 0.8401 0.091 1.008 1.216 0.082 368.72 0.9220 0.8444 1.091 1.251 0.025 357.35 0.3252 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 0.087 362.51 0.6885 0.5394 1.043 1.149 0.072 371.05 0.9797 0.9552 1.002 1.280 0.007 355.84 0.4565 0.3424 1.117 1.064 0.2113 1.134 1.081 0.100 379.66 0.8600 0.5739 1.018 1.338 0.	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
356.89 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 0.3525 0.2710 1.171 1.034 0.078 361.96 0.6597 0.5112 1.049 1.118 0.076 371.05 0.9797 0.9522 1.002 1.280 0.007 358.46 0.4088 0.3082 1.117 1.069 0.087 362.93 0.7081 0.5592 1.037 1.156 0.068 0.073 371.05 0.9797 0.952 1.002 1.280 0.007 355.90 0.218 0.0098 1.498 1.000 364.21 0.4661 0.213 1.114 1.010 1.010 380.98 0.8784 0.6022 1.0151 1.3161 0.050 <	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
357.31 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 0.087 362.93 0.7081 0.5592 1.037 1.156 0.068 0.007 379.66 0.8600 0.5739 1.018 1.338 0.056 355.90 0.0218 0.0098 1.467 0.996 0.017 366.42 0.553 0.2602 1.098 1.115 0.101 380.98 0.8784 0.6326 1.011 1.370 0.044 <t< td=""><td>356.89</td><td>0.2279</td><td>0.1786</td><td>1.247</td><td>1.013</td><td>0.060</td><td>360.91</td><td>0.6005</td><td>0.4573</td><td>1.066</td><td>1.117</td><td>0.082</td><td>367.73</td><td>0.8910</td><td>0.7921</td><td>1.008</td><td>1.236</td><td>0.031</td></t<>	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
357.75 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 1.117 1.069 0.087 362.93 0.7081 0.559 1.037 1.156 0.068 0.068 0.073 364.21 0.4661 0.2113 1.134 1.081 0.100 379.66 0.8600 0.5739 1.018 1.38 0.056 356.38 0.0454 0.0204 1.472 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 0.044 356.74 0.0551 0.020 1.467 0.996 0.017 366.42 0.5503 1.0621 1.157 0.101 </td <td>357.31</td> <td>0.2791</td> <td>0.2170</td> <td>1.220</td> <td>1.018</td> <td>0.069</td> <td>360.97</td> <td>0.6033</td> <td>0.4604</td> <td>1.066</td> <td>1.116</td> <td>0.082</td> <td>368.72</td> <td>0.9220</td> <td>0.8444</td> <td>1.009</td> <td>1.251</td> <td>0.025</td>	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
357.99 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 0.775 0.9552 1.002 1.280 0.007 358.94 0.4565 0.3424 1.117 1.069 0.087 362.93 0.7081 0.5592 1.037 1.156 0.068 Ethyl Butamate (1) + tert-Butanol (2) 355.90 0.0218 0.0094 1.472 0.996 0.014 365.28 0.5106 0.2352 1.112 1.010 0.101 380.98 0.8784 0.6082 1.015 1.361 0.050 356.71 0.0690 0.0310 1.455 0.998 0.024 367.45 0.5856 0.2835 1.087 1.131 0.100 382.66 0.9013 0.6579 1.011 1.382 0.042 357.31 0.1040 0.0470 <td>357.75</td> <td>0.3259</td> <td>0.2517</td> <td>1.195</td> <td>1.024</td> <td>0.074</td> <td>361.39</td> <td>0.6289</td> <td>0.4832</td> <td>1.059</td> <td>1.126</td> <td>0.080</td> <td>369.94</td> <td>0.9522</td> <td>0.8996</td> <td>1.003</td> <td>1.264</td> <td>0.014</td>	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
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 0.068 355.90 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 1.011 1.374 0.044 356.74 0.0555 0.0201 1.467 0.996 0.014 366.42 0.5585 1.087 1.115 0.101 381.96 0.8001 0.626 1.011 1.332 0.042 357.31 0.1040 0.0470 1.433 0.997 0.35 368.42 0.6169 0.3355 1.077 1.147 0.098 383.63 <td>357.99</td> <td>0.3552</td> <td>0.2710</td> <td>1.171</td> <td>1.034</td> <td>0.078</td> <td>361.96</td> <td>0.6597</td> <td>0.5112</td> <td>1.049</td> <td>1.138</td> <td>0.076</td> <td>371.05</td> <td>0.9797</td> <td>0.9552</td> <td>1.002</td> <td>1.280</td> <td>0.007</td>	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
358.94 0.4565 0.3424 1.117 1.069 0.087 362.93 0.7081 0.5592 1.037 1.156 0.068 55.90 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 0.044 357.31 0.1040 0.0470 1.433 0.997 0.35 368.42 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 <td>358.46</td> <td>0.4088</td> <td>0.3082</td> <td>1.140</td> <td>1.052</td> <td>0.084</td> <td>362.51</td> <td>0.6885</td> <td>0.5394</td> <td>1.043</td> <td>1.149</td> <td>0.072</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>	358.46	0.4088	0.3082	1.140	1.052	0.084	362.51	0.6885	0.5394	1.043	1.149	0.072						
Ethyl Butanote (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 0.055 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 0.0470 1.433 0.997 0.355 368.42 0.6169 0.3055 1.077 1.147 0.098 383.63 0.9105 0.6600 1.411 1.392 0.040 357.49 0.1201 0.0541 1.419 1.001 0.43 368.91 0.6322 0.3165 1.072 1.157 0.097 384.54 0.9204 0.7585<	358.94	0.4565	0.3424	1.117	1.069	0.087	362.93	0.7081	0.5592	1.037	1.156	0.068						
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 2.602 1.098 1.115 0.101 381.96 0.8901 0.6326 1.011 1.382 0.044 357.31 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 1.338 0.040 357.31 0.1040 0.0470 1.433 0.997 0.052 369.93 0.6619 0.3352 1.077 1.147 0.998 385.74 0.9204 0.758 1.010 1.402 0.036 <t< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td>Eth</td><td>yl Butaı</td><td>noate (1)</td><td>+ tert-</td><td>Butanol</td><td>(2)</td><td></td><td></td><td></td><td></td><td></td><td></td></t<>							Eth	yl Butaı	noate (1)	+ tert-	Butanol	(2)						
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 0.042 357.49 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 0.758 1.010 1.402 0.036 358.32 0.1628 0.0735 1.382 1.000 0.52 369.93 0.6619 0.3384 1.059 1.177 0.093 385.74 0.9320 0.7369 1.004 1.423 0.024 <t< td=""><td>355.90</td><td>0.0218</td><td>0.0098</td><td>1.498</td><td>1.000</td><td>0.009</td><td>364.21</td><td>0.4661</td><td>0.2113</td><td>1.134</td><td>1.081</td><td>0.100</td><td>379.66</td><td>0.8600</td><td>0.5739</td><td>1.018</td><td>1.338</td><td>0.056</td></t<>	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
356.54 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 0.042 357.49 0.1201 0.0541 1.419 1.001 0.043 368.42 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 1.077 1.147 0.098 385.74 0.9204 0.758 1.010 1.402 0.036 358.85 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 0.029 <	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
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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
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 0.66098 0.3322 1.051 1.114 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 0.7311 0.0393 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 0.84 373.55 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 0.089 377.45 0.7010 1.466 1.026 1.276 0.071 390.22 0.9720 0.8731 1.004 1.443 0.014 <	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
358.850.19830.08871.3441.0070.064371.030.69080.36321.0511.1940.089386.870.94240.76851.0041.4230.024359.440.23090.10321.3151.0110.072372.630.73010.39931.0381.2240.082387.840.95100.79611.0021.4320.019360.200.27970.12311.2621.0270.084373.550.75140.42071.0321.2440.078388.930.96060.82951.0011.4430.016361.130.32460.14311.2241.0350.089375.450.79010.46661.0261.2760.071390.220.97200.87311.0041.4570.014362.370.38710.17041.1721.0570.095377.060.81950.50761.0231.3010.066391.060.97800.89751.0021.4620.010363.430.43120.19391.1551.0660.098378.520.84250.54411.0201.3190.060392.070.98550.92991.0011.4750.007	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
359.440.23090.10321.3151.0110.072372.630.73010.39931.0381.2240.082387.840.95100.79611.0021.4320.019360.200.27970.12311.2621.0270.084373.550.75140.42071.0321.2440.078388.930.96060.82951.0011.4430.016361.130.32460.14311.2241.0350.089375.450.79010.46661.0261.2760.071390.220.97200.87311.0041.4570.014362.370.38710.17041.1721.0570.095377.060.81950.50761.0231.3010.066391.060.97800.89751.0021.4620.010363.430.43120.19391.1551.0660.098378.520.84250.54411.0201.3190.060392.070.98550.92991.0011.4750.007	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
360.200.27970.12311.2621.0270.084373.550.75140.42071.0321.2440.078388.930.96060.82951.0011.4430.016361.130.32460.14311.2241.0350.089375.450.79010.46661.0261.2760.071390.220.97200.87311.0041.4570.014362.370.38710.17041.1721.0570.095377.060.81950.50761.0231.3010.066391.060.97800.89751.0021.4620.010363.430.43120.19391.1551.0660.098378.520.84250.54411.0201.3190.060392.070.98550.92991.0011.4750.007	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
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	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
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	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
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 0.9855 0.9299 1.001 1.475 0.007 0.9855 0.9299 0.9855 0.98	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 $z_1 z_2 \equiv z(1 - z)$ instead of $x_1 x_2 \equiv x(1 - x)$ 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

$$\frac{G_{\rm m}^{\rm E}}{RT}(T, x_1) = z_1 z_2 \sum_{i=0}^{m} A_i z_1^{\ i}$$
(4)

with the A_i coefficients being treated as temperaturedependent by means of the relation

$$A_{i} = A_{i1}T + \frac{A_{i2}}{T} + A_{i3}$$
(5)

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

$$C_{\rho}^{\rm E} = \left(\frac{\partial H_{\rm m}^{\rm E}}{\partial T}\right)_{p,x} \qquad -\frac{H_{\rm m}^{\rm E}}{RT} = T \left[\frac{\partial (G_{\rm m}^{\rm E}/RT)}{\partial T}\right]_{p,x} \tag{6}$$

the excess Gibbs energy function can be written as

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

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 (**A**) and γ_i vs x_1 (**O**) for the binary mixtures $C_{u-1}H_{2u-1}COOC_2H_5$ (1) + CH₃(CH₃)C(OH)CH₃ (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.

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

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,

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

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, ..., 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, ..., n on one hand and $\{x_{1i}, (H_m^E/RT_i)_i\}$; i = 1, ..., 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, 12

parameters	1	2	3	4
A01	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
<i>k</i> _g	0.989	0.671	0.985	0.789
$s(G_{\rm m}^{\rm E}/RT)$	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)
$s(H_{\rm m}^{\rm E}/RT)$ at	0.020 (0.99)	0.012 (0.99)	0.013 (0.99)	0.011 (0.99)
299.15 K $s(H_{\rm m}^{\rm E}/RT)$ at	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) + tertbutanol (2); and 4, ethyl butanoate (1) + tert-butanol (2).

excess enthalpies measured at a concentration of the reference component, that is, the first component, $x_{1,i}$, 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

$$OF = \sum_{i=1}^{q} \left[\frac{H_{m}^{E}}{RT} (T_{j}, x_{1j}) - \left(\frac{H_{m}^{E}}{RT_{j}} \right)_{j} \right]^{2} + \sum_{j=1}^{n} \left[\ln \gamma_{1} (T_{j}, x_{1j}) - \ln \gamma_{1j} \right]^{2} + \sum_{j=1}^{n} \left[\ln \gamma_{2} (T_{j}, x_{1j}) - \ln \gamma_{2j} \right]^{2}$$
(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 $H_{\rm m}^{\rm E}$ and $V_{\rm m}^{\rm E}$ 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 socalled active fraction and temperature. The most suitable final expression was

$$\frac{G_{\rm m}^{\rm E}}{RT}(T,x_1) = z_1(x_1)\left[\left(\frac{A_{01}}{T} + A_{02}\right) + \left(\frac{A_{21}}{T} + A_{22}\right)z_1^{\ 2}(x_1)\right] (11)$$

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
- $H_{\rm m}^{\rm E} = {\rm excess~enthalpy}$
- $G_{\rm m}^{\rm E} = {\rm excess} {\rm ~Gibbs~function}$
- p = absolute pressure
- $p_i^0 =$ vapor pressure
- R = gas constant
- r^2 = correlation coefficient on *Y*-function, $r^2 = \sum (Y_{cal}$ $\overline{Y}^{2/}[\Sigma(Y_{cal} - \overline{Y})^{2} + \Sigma(Y_{cal} - Y_{exp})^{2}]$ s = standard deviation on Y-function, s = $[\Sigma(Y_{exp} - Y_{exp})^{2}]$
- $(N n)^{1/2}$
- T = temperature
- $V_{\rm m}^{\rm E} = {\rm excess \ volume}$
- $x_i =$ 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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