Vapor−Liquid Equilibria for Binary Systems Composed of a Propyl Ester (Ethanoate, Propanoate, Butanoate) + an *n*-Alkane (C_7, C_9)

Juan Ortega,* Carmelo González, and Salvador Galván

Laboratorio de Termodinámica y Fisicoquímica, Escuela Superior de Ingenieros Industriales, Universidad de Las Palmas de Gran Canaria, 35071-Las Palmas de Gran Canaria, Islas Canarias, Spain

This paper reports isobaric vapor−liquid equilibrium measurements made using a small equilibrium still at a pressure of 101.32 kPa and other excess properties for a set of six binary mixtures composed of one of three propyl esters (ethanoate, propanoate, butanoate) and one of two *n*-alkanes (heptane, nonane). The vapor pressures for the *n*-alkanes measured using the same equilibrium still and the correlations calculated are also presented. Application of the point-to-point test showed the systems studied to be consistent. All the data were correlated, and processing of the equilibrium data included the excess enthalpies. The system consisting of propyl ethanoate + heptane has an azeotrope at $x_{az} = 0.423$, $T_{az} =$ 366.9 K, and the system consisting of propyl butanoate + nonane has an azeotrope at $x_{az} = 0.726$, $T_{az} =$ 414.4 K. Both the modified-UNIFAC theoretical model and the Nitta model yield acceptable estimates of the different properties for these propyl ester + *n*-alkane mixtures.

Introduction

In the context of ongoing work that has been carried out by our research team for a number of years focusing on analyzing the behavior of binary systems all sharing an alkyl ester as a common component, this paper considers the isobaric vapor−liquid equilibrium (VLE) and other properties of mixtures composed of a propyl ester + an *n*-alkane. On the basis of the experimental VLE values and the excess molar quantities, the enthalpies, H_m^E, and volumes, V_m^E, obtained for a large number of ester + *n*-alkane and ester + *n*-alkanol systems, our team has established a comprehensive database of thermodynamic values. Still, we are aware that our database contains certain gaps in the VLE values for certain ester + *n*-alkane mixtures, and the literature likewise does not contain very many studies dealing with such systems. In this connection, in an earlier paper Galván et al.[1] published values for propyl methanoate + an *n*-alkane (C_7−C_9), and Gmehling et al.[2] (Vol. I/5, pp 329, 514) set out experimental isobaric VLE values for ester + *n*-alkane mixtures. However, the only literature values for propyl esters found were isothermic VLE values for propyl ethanoate + hexane published by Slavin and Abramzon.[3]

Therefore, to complete the task already undertaken by our team and to make available additional values in the literature, this paper presents the isobaric VLE values for systems composed of a propyl ester (ethanoate, propanoate, butanoate) and one of two *n*-alkanes (heptane, nonane). As already stated above, no VLE values for these systems have been disclosed in the literature other than azeotropic points for the mixture propyl ethanoate + heptane measured by Gmehling and Bölts,[4] which have been compared with the results of our study. Additionally, to complete this work on phase equilibria and contribute to an analysis of the thermodynamic behavior of the experimental systems, the excess quantities for these mixtures were also measured, and the H_m^E values were then used in the treatment of the VLE values.

Finally, certain group-contribution models, namely, the versions of the UNIFAC model published by Hansen et al.[5] and Gmehling et al.,[6] the ASOG model of Tochigi et al.,[7] and the model of Nitta et al.,[8] were employed to test the theoretical predictions of the VLE values for the systems studied here.

Experimental Section

Materials. The propyl esters used in the experiment were of the purest commercial grade from Aldrich; the *n*-alkanes were from Fluka. All components were degassed ultrasonically and then dried on a molecular sieve (Fluka, type 3A) before use. Component purity was verified by GC using a model HP-6890 apparatus with FID. The level of purity obtained is set out in Table 1 and was in all cases in consonance with the manufacturers' specifications. Component quality was also checked by measuring certain properties experimentally, that is, the normal boiling point $T_{b,i}^{\circ}$, density, ρ, and refractive index, n_D, at 298.15 K. The values recorded are presented in Table 1 for all the components and showed acceptable agreement with the literature values in all cases.

Apparatus and Procedure. The experimental equipment used to measure the isobaric VLE values was an equilibrium still in which both phases were refluxed. A diagram of the main unit was published some years ago by Ortega et al.[13] The pressure of the installation was regulated by a Desgranges et Huot model PPC2 pressure controller/calibrator with an uncertainty of ±0.02 kPa. The temperature for each equilibrium stage was taken using a model ASL-F25 thermometer periodically calibrated in accordance with ITS-90, and the precision of the reading was ±10 mK.

Equilibrium concentrations for propyl ester (1) + *n*-alkane (2) mixtures were calculated from the density−concentration curve using second-degree polynomial equations at 298.15 K which were previously determined using mixtures of known composition. The relations $\rho = \rho(x_1)$ were validated by verifying the quality of the results for

10.1021/je000358a CCC: $20.00

Table 1. Physical Properties of Pure Substances, *n*-Alkanes and Propyl Esters, Obtained Experimentally

compound	supplier	mass fraction	$T^{\circ}_{b,i}$/K		ρ(298.15 K)/kg·m^{-3}		n_D at 298.15 K	
			exp	lit.	exp	lit.	exp	lit.
n-heptane	Fluka	0.99	371.49	371.57[a] 371.55[d]	679.27	679.46[a] 679.51[d]	1.3851	1.38511[a] 1.3851[d]
n-nonane	Fluka	0.99	423.53	423.97[a]	713.85	713.75[a] 713.81[d]	1.4030	1.40311[a] 1.40338[d]
propyl ethanoate	Aldrich	0.99	374.55	374.69[a] 374.65[b]	882.55	883.03[a] 882.60[b]	1.3816	1.3828[a,b] 1.3817[d]
propyl propanoate	Aldrich	>0.99	395.55	395.65[b,c]	876.55	876.70[b] 876.82[c]	1.3906	1.3920[b,c]
propyl butanoate	Aldrich	>0.99	416.41	416.45[b,c]	867.92	868.20[b] 868.04[c]	1.3975	1.3976[b,c]

[a] Riddick et al.[9] [b] TRC a-5000.[10] [c] Daubert and Danner.[11] [d] Timmermans.[12]

V^E_m on x_1, and those were used in the inverse calculus with the known densities for the condensed vapor and the liquid to determine both phase concentrations at equilibrium, which were estimated to be better than ±0.002 ester mole fraction units.

Results and Discussion

Densities and Excess Volumes. As part of our research program on binary ester + *n*-alkane systems, in a previous paper Ortega et al.[14] published the measurements for H^E_m and V^E_m for mixtures consisting of a propyl ester + an *n*-alkane. However, when measuring the isobaric VLE data by the method described in the preceding section, the density–concentration curves for each of the mixtures were redetermined. Table 2 sets out the new values together with the V^E_m values at the same concentration for each of the binary systems composed of one of the propyl esters (1) + one of the *n*-alkanes (2) considered here at temperature of (298.15 ± 0.02) K. The results of V^E_m on x_1 were correlated using the polynomial equation

$$Y^E_m = x_1(1 - x_1)\sum_{i=1}^{N} b_{i-1}{z_1}^{i-1} \qquad (1)$$

where $Y^E_m = 10^9 V^E_m/(\text{m}^3\cdot\text{mol}^{-1})$ and $z = x_1/(x_1 + kx_2)$, substituting k by k_v in the fitting excess volumes and taking a constant value of $k_v = V^{\circ}_2/V^{\circ}_1$, V°_i being the molar volumes for the pure components (taken from Table 1) in the mixtures at the working temperature (see ref 15). Table 3 presents the values for the coefficients b_i in eq 1 and the standard deviations, $s(V^E_m)$, for each mixture. The excess equimolar values have been plotted versus the number of carbon atoms in the acid chain on the propyl ester in Figure 1, together with literature values for comparison. The values for the systems composed of propyl methanoate + an *n*-alkane (C_7, C_9) from Ortega et al.[19] have also been plotted in the interest of better depicting the trend with ester chain length. The figure shows that the equimolar values obtained in the present study were in good agreement with other literature values.[14,16–18] The largest differences were less than 5%, were for the mixtures propyl propanoate + heptane and propyl propanoate + nonane measured at our laboratory, and were slightly lower than the values presented here.

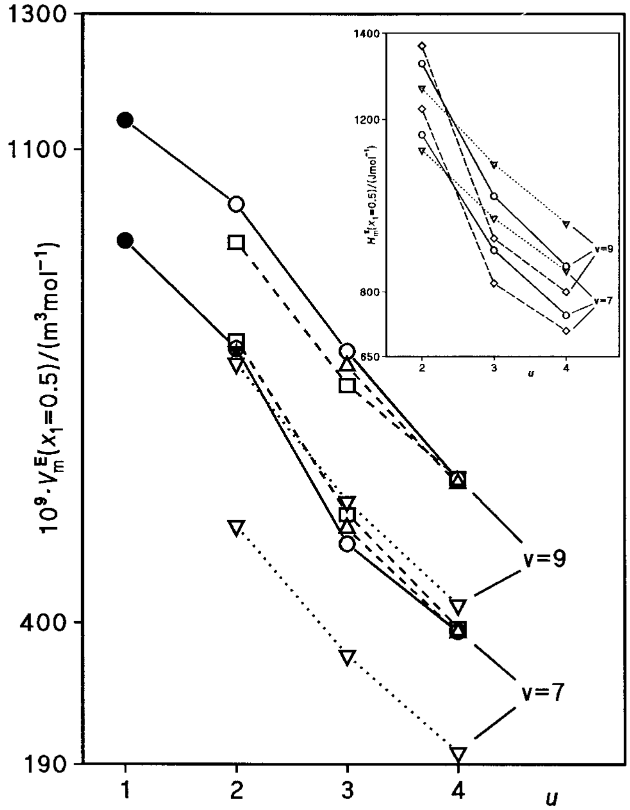

Figure 1. Representation of equimolar values of V^E_m obtained in this work (○) for mixtures {$H_{2u-1}C_{u-1}COO(CH_2)_2CH_3$ (u = 1–4) + C_vH_{2v+2} (v = 7, 9)}. Comparison with experimental values from the literature and those obtained by theoretical models: (★) Dusart et al.;[16] (△) Lorenzana et al.;[17,18] (□) Ortega et al.;[14] (●) Ortega et al.;[19] (▽) calculated by Nitta et al..[8] The inset represents the excess equimolar enthalpies for the same mixtures and those calculated by Nitta et al.[8] (▽) and by Gemhling et al.[6] (◇).

The enthalpies for the systems considered had already been measured by Ortega et al.[14] in a previous study. However, Table 3 gives the values of the coefficients for the nondimensional correlations of the excess enthalpies, H^E_m/RT, similar to eq 1 but now writing k_h instead k for the mixtures consisting of a propyl ester + (C_7,C_9) required for processing the VLE data. In this study, the values of k_h were determined by optimization as part of the regression of the (x_1, H^E_m) values using a least-squares procedure. The experimental equimolar values for H^E_m and the changes in those values with the different mixture components are shown in the inset in Figure 1. Ortega et al.[14,19] set out a detailed analysis of the behavior of these mixtures, but even so, some explanation of the values in Figure 1 would seem to be called for. The V^E_m values increased with *n*-alkane chain length, as a result of intensification of the van der Waals attractions, whereas the V^E_m values and the H^E_m values as well both decreased with the number of CH_2 groups on the acid portion of the ester, because of the decrease in the dipole moments of the propyl ester and the decrease in the dipole–dipole interactions.

Table 2. Densities, ρ, and Excess Volumes, V_m^E, for Binary Systems of Propyl Esters (1) + an *n*-Alkane (2) at 298.15 K

x_1	ρ / $\mathrm{kg \cdot m^{-3}}$	$10^9 V_m^E$ / $\mathrm{m^3 \cdot mol^{-1}}$	x_1	ρ / $\mathrm{kg \cdot m^{-3}}$	$10^9 V_m^E$ / $\mathrm{m^3 \cdot mol^{-1}}$
Propyl Ethanoate (1) + Heptane (2)					
0.0000	679.27	0	0.6075	786.86	741
0.0375	684.36	168	0.6473	795.53	709
0.1199	696.92	395	0.6507	796.27	708
0.1334	699.08	419	0.6914	805.52	647
0.1892	708.06	537	0.7813	826.66	512
0.2610	720.06	665	0.8047	832.40	468
0.2827	723.81	692	0.8547	845.07	352
0.3533	736.26	784	0.8824	852.13	301
0.4186	748.45	813	0.9082	858.87	250
0.4554	755.25	819	0.9408	867.71	155
0.5053	765.50	803	0.9892	881.06	33
0.5214	768.79	795	1.0000	882.55	0
0.5697	778.79	772			
Propyl Ethanoate (1) + Nonane (2)					
0.0000	713.85	0	0.5797	787.76	991
0.0216	715.88	83	0.6429	799.09	931
0.0607	719.70	219	0.6933	808.76	860
0.1119	724.73	424	0.7526	820.84	759
0.1735	731.39	590	0.8189	835.60	589
0.2985	743.20	850	0.8548	844.05	492
0.3407	751.55	934	0.8924	853.25	395
0.4296	763.96	997	0.9673	873.17	138
0.5097	776.15	1018	1.0000	882.55	0
Propyl Propanoate (1) + Heptane (2)					
0.0000	679.27	0	0.5702	783.83	491
0.0156	681.20	46	0.7177	814.45	392
0.0475	686.51	132	0.7531	822.08	346
0.1368	701.82	317	0.8269	838.12	264
0.2142	715.61	413	0.8809	850.10	195
0.2978	730.89	487	0.9313	861.53	116
0.3625	743.09	506	0.9591	867.89	73
0.4298	755.98	524	0.9867	874.25	31
0.4814	766.05	525	1.0000	876.55	0
Propyl Propanoate (1) + Nonane (2)					
0.0000	713.85	0	0.5985	794.59	762
0.0189	715.96	38	0.6645	806.12	697
0.0627	720.70	189	0.7125	814.91	633
0.0828	722.70	268	0.8014	832.05	494
0.1964	736.34	517	0.8207	835.94	458
0.2600	744.36	632	0.9012	853.06	260
0.3197	752.29	706	0.9058	854.06	252
0.4005	763.58	781	0.9381	861.31	161
0.4805	775.55	798	0.9626	866.84	104
0.5187	781.50	800	1.0000	876.55	0
Propyl Butanoate (1) + Heptane (2)					
0.0000	679.27	0	0.5511	782.02	376
0.0386	686.29	79	0.5932	789.99	364
0.0723	692.45	141	0.6088	792.97	352
0.1249	702.15	214	0.6833	807.11	319
0.1735	711.12	274	0.7336	816.73	280
0.2043	716.85	298	0.7856	826.64	244
0.2442	724.30	328	0.7966	828.79	228
0.3159	737.72	362	0.8684	842.59	155
0.4034	754.14	385	0.9169	851.91	102
0.4827	769.05	393	0.9787	863.85	24
0.5161	775.38	386	1.0000	867.92	0
Propyl Butanoate (1) + Nonane (2)					
0.0000	713.85	0	0.5791	793.30	592
0.0223	716.40	80	0.6455	804.07	539
0.1616	733.62	376	0.7123	815.32	459
0.2297	742.49	477	0.7706	825.36	392
0.2802	749.30	532	0.8149	833.21	327
0.3866	764.22	599	0.8818	845.42	217
0.4310	770.68	614	0.9402	856.23	141
0.5030	781.46	617	1.0000	867.92	0

Table 3. Coefficients and Standard Deviation, *s*, Obtained Using Eq 1 To Correlate the Excess Properties, V_m^E and H_m^E/RT

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

binary mixture	k_v	b_0	b_1	$10^9 s(V_m^E)$/ $\mathrm{m^3 \cdot mol^{-1}}$
propyl ethanoate (1) +				
heptane (2)	1.274	3685	−989	11
nonane (2)	1.553	4134	−141	9
propyl propanoate (1) +				
heptane (2)	1.111	2581	−976	12
nonane (2)	1.354	3369	−405	9
propyl butanoate (1) +				
heptane (2)	0.983	1948	−726	8
nonane (2)	1.198	2851	−848	10

$q^h = H_m^E/RT$

binary mixture	k_h	A_0^1	A_1^1	$10^3 s(q^h)$
propyl ethanoate (1) +				
heptane (2)	0.19	2.379	−0.581	4
nonane (2)	0.02	3.396	−1.267	4
propyl propanoate (1) +				
heptane (2)	0.19	1.788	−0.403	2
nonane (2)	0.10	1.907	−0.288	2
propyl butanoate (1) +				
heptane (2)	0.18	1.600	−0.419	1
nonane (2)	0.18	1.727	−0.410	3

Vapor Pressures. Because of the influence of the vapor pressures on the processing of the VLE values, in our papers we have presented values for that quantity, p_i° for the components used in this study, measured using the same experimental VLE equipment. The vapor pressures for the propyl esters propanoate, butanoate, and ethanoate were published, respectively, in a previous paper by González et al.,[20] and for that reason this paper only presents the measurements carried out for the *n*-alkanes heptane and nonane over a range of pressures within the tolerance of the glass ebulliometer. Table 4 gives the direct experimental values, and Table 5 relates the constants in the Antoine equation employed in correlating the (T, p_i°) values

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

for each of the working components. The values of the constants A, B, and C for the esters in Table 5 have been taken from previous works mentioned above and were also used in the calculations of the VLE data. Figure 2 depicts the vapor pressure regression lines for the *n*-alkane on reduced coordinates, correlating the temperature−vapor pressure value pairs using an equation similar to eq 2. Although the constants in a reduced form of the Antoine equation (designated a, b, and c) are related in simple fashion with the constants in eq 1 (see ref 24), here a separate regression was performed for the reduced quantities (T_r, $p_{i,r}^\circ$), with minimization of the standard deviations $s(p_{i,r}^\circ)$. The values obtained for a, b, and c did not differ very much from the values calculated using the constant values for eq 2 and are also shown in Table 5 together with the values of the acentric factors ω, calculated for each of the components using the definition of Pitzer, and those values were used in subsequent calculations of the VLE values. There was good agreement between the values of ω obtained in this study and the literature values.

Presentation of VLE Data. The T, x_1, and y_1 values were determined once the equilibrium between the two phases liquid and vapor had been reached, at the pressure $p = (101.32 \pm 0.02)$ kPa for the six binary mixtures considered here and represented empirically as $\{H_{2u-1}C_{u-1}COO(CH_2)_2CH_3$ ($u = 2-4$) (1) + C_vH_{2v+2} ($v =$

Table 4. Experimental Vapor Pressures, p_i°, for Pure *n*-Alkanes

T/K	p_i°/kPa	T/K	p_i°/kPa	T/K	p_i°/kPa
Heptane					
328.27	22.93	362.34	77.28	380.66	133.31
329.40	24.21	363.40	80.01	381.33	136.00
332.05	26.68	364.45	82.61	382.04	138.66
334.44	29.27	365.50	85.29	382.74	141.32
336.77	31.99	366.44	87.93	383.42	143.96
338.90	34.74	367.49	90.63	384.05	146.65
340.84	37.30	368.43	93.36	384.71	149.32
342.85	40.02	369.36	95.98	385.36	152.02
344.59	42.67	370.28	98.64	386.00	154.66
346.24	45.33	371.49	101.32	386.64	157.31
347.94	48.09	372.02	103.91	387.26	159.98
349.55	50.69	372.90	106.59	387.87	162.64
351.02	53.45	373.72	109.24	388.48	165.27
352.54	55.93	374.58	112.01	389.07	167.97
353.96	58.75	375.38	114.64	389.66	170.67
355.13	61.42	376.19	117.33	390.24	173.33
356.40	64.02	376.94	119.96	390.81	175.93
357.69	66.65	377.68	122.57	391.36	178.65
358.85	69.32	378.47	125.32	391.94	181.31
360.11	72.05	379.21	127.98	393.04	186.65
361.23	74.63	379.94	130.64		
Nonane					
403.02	56.66	422.95	99.79	428.67	115.84
404.08	58.47	423.10	100.16	429.60	118.64
405.99	61.91	423.24	100.49	430.49	121.43
406.77	63.39	423.35	100.81	431.33	123.97
408.72	67.03	423.47	101.12	431.87	125.98
410.40	70.43	423.51	101.29	433.35	130.81
412.03	73.78	423.53	101.32	434.18	133.49
413.52	76.99	424.37	103.46	435.05	136.17
415.08	80.47	424.43	103.74	435.83	138.85
416.25	83.28	424.51	103.88	436.59	141.43
417.68	86.76	424.60	104.31	437.27	143.81
419.18	90.06	424.98	105.32	437.98	146.36
420.58	93.54	425.50	106.67	438.67	148.77
421.63	96.31	425.85	107.76	439.18	150.76
422.40	98.28	426.89	110.71		
422.77	99.35	427.79	113.26		

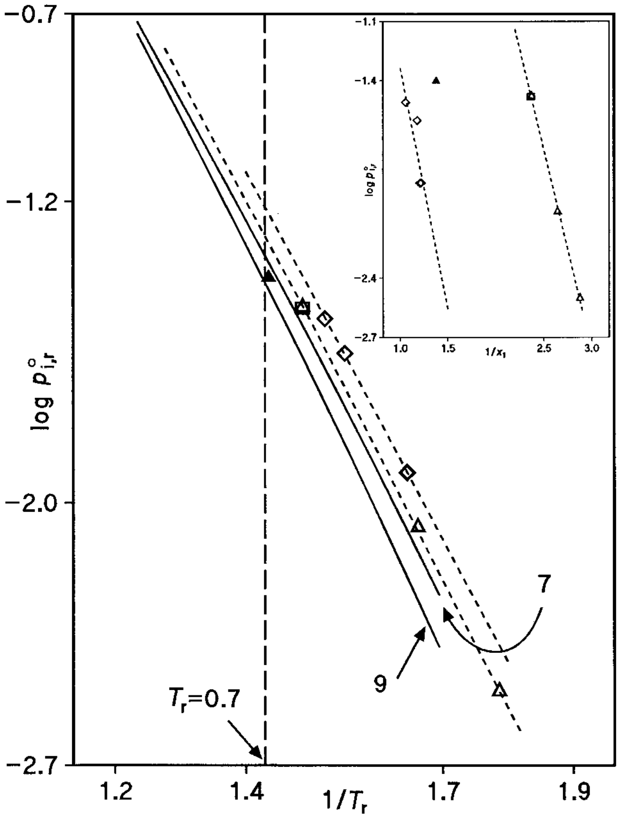

Figure 2. Vapor pressure lines in reduced coordinates for heptane (7) and nonane (9) calculated using the coefficients of Table 5. For propyl ethanoate + heptane: experimental azeotropes (□); others from Gmehling et al.[21] (△) and the azeotropic line (- - -), $\log(p_{i,r}^\circ/\text{kPa}) = 2.305 - 2.019/(T_r - 0.139)$. For propyl butanoate + nonane: experimental azeotrope (▲). For ethyl ethanoate + heptane: azeotropes from Gmehling et al.[21] (◇); azeotropic line (- - -), $\log(p_{i,r}^\circ/\text{kPa}) = 2.421 - 3.369/(T_r - 0.126)$. The inset figure plots the same azeotropes as a function of ester concentration.

Table 5. Coefficients of Antoine Equation

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

compound	A	B	C	$s(p_i^\circ)$/kPa	ΔT/K	refs
propyl ethanoate	6.51160	1524.56	36.19		320−430	20
propyl propanoate	6.06539	1301.06	75.11		360−420	20
propyl butanoate	6.60941	1723.42	42.02		375−440	20
n-heptane	6.10457	1296.68	54.81	0.08[c]	320−400	this work
	6.02167	1264.90	56.61			9
	6.02743	1267.83	56.33		300−375	22
	6.01876	1264.37	56.51		270−400	2
n-nonane	5.79182	1241.80	95.54	0.08[c]	400−450	this work
	6.06383	1431.82	71.14			9
	6.06254	1430.46	71.34		340−425	22
	6.05932	1429.46	71.33		234−452	2

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

compound	a	b	c	ω	refs
propyl ethanoate	2.9770	2.7670	0.070	0.4150	this work
				0.3941	11
propyl propanoate	2.5945	2.2752	0.127	0.3761	this work
				0.3762	11
propyl butanoate	3.3104	3.0886	0.051	0.4486	this work
				0.4484	11
n-heptane	2.6559	2.3870	0.103	0.3424	this work
				0.349	23
				0.349	11
n-nonane	2.4512	2.1091	0.158	0.4401	this work
				0.445	23
				0.4368	11

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

Table 6. Experimental Data, $T-x_1-y_1$, and Calculated Quantities for the VLE of the Binary Mixtures of Propyl *n*-Alkanoate (1) + *n*-Alkanes (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2	G^E_m/RT	T/K	x_1	y_1	γ_1	γ_2	G^E_m/RT
Propyl Ethanoate (1) + Heptane (2)											
371.49	0.0000	0.0000		1.000	0.000	367.42	0.5786	0.5180	1.108	1.287	0.165
371.22	0.0126	0.0246	2.151	0.994	0.004	367.70	0.6145	0.5406	1.079	1.330	0.157
370.34	0.0428	0.0728	1.930	1.003	0.031	368.02	0.6570	0.5740	1.061	1.374	0.148
369.40	0.0961	0.1494	1.814	1.000	0.057	368.42	0.6910	0.6038	1.048	1.402	0.137
368.94	0.1291	0.1866	1.710	1.006	0.074	368.86	0.7247	0.6368	1.040	1.425	0.126
368.42	0.1727	0.2326	1.618	1.014	0.094	369.40	0.7715	0.6813	1.029	1.484	0.112
367.93	0.2140	0.2753	1.568	1.022	0.113	370.05	0.8090	0.7232	1.021	1.514	0.096
367.59	0.2589	0.3185	1.515	1.029	0.129	370.73	0.8439	0.7652	1.015	1.542	0.080
367.34	0.3014	0.3514	1.447	1.047	0.143	371.35	0.8829	0.8145	1.013	1.597	0.067
367.07	0.3416	0.3810	1.395	1.068	0.157	372.02	0.9129	0.8528	1.006	1.673	0.050
367.02	0.3713	0.4016	1.355	1.083	0.163	372.51	0.9392	0.8954	1.012	1.680	0.043
367.00	0.4043	0.4110	1.274	1.126	0.168	373.12	0.9611	0.9285	1.007	1.765	0.029
367.00	0.4344	0.4304	1.242	1.146	0.171	373.40	0.9784	0.9599	1.014	1.770	0.026
367.03	0.4666	0.4505	1.209	1.172	0.173	373.72	0.9875	0.9764	1.013	1.784	0.020
367.10	0.5072	0.4729	1.165	1.214	0.173	374.17	0.9958	0.9917	1.007	1.845	0.009
367.23	0.5408	0.5007	1.152	1.230	0.172	374.55	1.0000	1.0000	1.000		0.000
Propyl Ethanoate (1) + Nonane (2)											
423.53	0.0000	0.0000		1.000	0.000	385.35	0.5256	0.8118	1.140	1.187	0.150
421.15	0.0081	0.0539	2.079	1.013	0.018	384.10	0.5685	0.8313	1.117	1.219	0.148
418.00	0.0241	0.1439	1.985	1.010	0.026	382.70	0.6104	0.8519	1.108	1.241	0.147
415.19	0.0436	0.2224	1.804	1.008	0.033	381.35	0.6829	0.8735	1.054	1.364	0.134
412.27	0.0696	0.3035	1.649	1.003	0.038	380.55	0.7051	0.8832	1.055	1.391	0.135
409.05	0.0980	0.3713	1.542	1.020	0.060	379.35	0.7628	0.9032	1.032	1.493	0.119
405.23	0.1464	0.4632	1.409	1.025	0.071	378.50	0.7907	0.9154	1.033	1.523	0.114
400.84	0.2037	0.5567	1.352	1.030	0.085	377.55	0.8357	0.9310	1.021	1.637	0.099
399.51	0.2230	0.5791	1.328	1.042	0.095	376.86	0.8610	0.9414	1.023	1.680	0.091
395.82	0.2793	0.6413	1.288	1.070	0.119	376.23	0.9033	0.9572	1.009	1.807	0.065
395.05	0.2958	0.6559	1.268	1.075	0.121	375.79	0.9311	0.9666	1.001	2.008	0.049
393.28	0.3254	0.6842	1.258	1.087	0.131	375.47	0.9451	0.9720	1.001	2.138	0.043
391.72	0.3562	0.7111	1.244	1.094	0.136	375.12	0.9711	0.9840	0.996	2.354	0.021
389.85	0.4061	0.7425	1.196	1.122	0.141	374.79	0.9836	0.9901	0.999	2.595	0.015
388.67	0.4272	0.7597	1.201	1.127	0.147	374.55	1.0000	1.0000	1.000		0.000
387.27	0.4707	0.7827	1.165	1.153	0.148						
Propyl Propanoate (1) + Heptane (2)											
371.49	0.0000	0.0000		1.000	0.000	382.83	0.7148	0.5238	1.060	1.218	0.098
371.03	0.0020	0.0020	2.042	1.004	0.005	383.49	0.7401	0.5508	1.055	1.240	0.096
371.16	0.0210	0.0193	1.933	1.002	0.015	384.16	0.7570	0.5725	1.051	1.241	0.090
371.40	0.0520	0.0445	1.777	1.001	0.031	384.85	0.7747	0.5945	1.045	1.247	0.084
372.41	0.1395	0.1016	1.464	1.008	0.060	385.80	0.8098	0.6429	1.051	1.270	0.086
373.19	0.2192	0.1494	1.335	1.029	0.086	386.55	0.8213	0.6578	1.037	1.271	0.072
374.18	0.2997	0.1975	1.250	1.054	0.103	387.35	0.8433	0.6867	1.030	1.300	0.066
374.55	0.3365	0.2177	1.213	1.073	0.112	388.28	0.8630	0.7217	1.029	1.291	0.060
375.19	0.3943	0.2526	1.176	1.103	0.124	389.22	0.8848	0.7549	1.022	1.321	0.051
376.36	0.4633	0.3048	1.164	1.122	0.132	390.17	0.9057	0.7915	1.018	1.340	0.044
376.75	0.4787	0.3148	1.149	1.127	0.129	391.12	0.9258	0.8277	1.014	1.375	0.036
377.27	0.5062	0.3367	1.143	1.135	0.130	391.81	0.9395	0.8558	1.013	1.389	0.032
378.61	0.5681	0.3818	1.107	1.167	0.125	392.62	0.9511	0.8765	1.001	1.443	0.019
379.73	0.6062	0.4188	1.099	1.168	0.118	393.55	0.9671	0.9108	0.997	1.513	0.011
380.50	0.6399	0.4473	1.086	1.190	0.116	394.00	0.9735	0.9277	0.996	1.510	0.007
381.01	0.6595	0.4671	1.083	1.197	0.114	394.57	0.9818	0.9460	0.991	1.621	0.000
382.10	0.6912	0.5002	1.070	1.204	0.104	395.55	1.0000	1.0000	1.000		0.000
Propyl Propanoate (1) + Nonane (2)											
423.53	0.0000	0.0000		1.000	0.000	406.94	0.3333	0.5399	1.199	1.071	0.107
422.82	0.0055	0.0259	2.388	0.997	0.002	406.24	0.3540	0.5592	1.191	1.080	0.112
422.20	0.0092	0.0500	2.769	0.991	0.001	405.23	0.3890	0.5928	1.179	1.086	0.114
421.23	0.0246	0.0868	1.850	0.992	0.007	404.45	0.4181	0.6136	1.158	1.107	0.120
420.45	0.0343	0.1105	1.716	0.996	0.014	403.55	0.4524	0.6408	1.144	1.122	0.124
419.65	0.0456	0.1331	1.586	1.002	0.023	402.80	0.4843	0.6649	1.131	1.135	0.125
418.69	0.0666	0.1748	1.458	1.000	0.025	402.00	0.5226	0.6915	1.113	1.156	0.125
418.25	0.0718	0.1841	1.439	1.006	0.031	401.38	0.5590	0.7144	1.093	1.180	0.123
417.24	0.0912	0.2196	1.384	1.008	0.037	400.77	0.5860	0.7347	1.090	1.188	0.122
416.75	0.1005	0.2382	1.378	1.007	0.039	399.85	0.6321	0.7655	1.079	1.214	0.119
416.35	0.1077	0.2487	1.356	1.012	0.044	399.33	0.6689	0.7862	1.062	1.249	0.114
415.67	0.1186	0.2688	1.352	1.015	0.049	398.70	0.7079	0.8106	1.052	1.279	0.108
414.95	0.1331	0.2892	1.320	1.023	0.056	398.11	0.7567	0.8384	1.034	1.333	0.096
413.75	0.1587	0.3286	1.294	1.028	0.064	397.62	0.7937	0.8622	1.028	1.361	0.085
413.06	0.1730	0.3513	1.290	1.029	0.068	397.11	0.8348	0.8870	1.019	1.415	0.073
412.63	0.1875	0.3715	1.273	1.027	0.067	396.71	0.8609	0.9060	1.021	1.416	0.066
411.09	0.2246	0.4221	1.253	1.032	0.075	396.30	0.8951	0.9262	1.015	1.492	0.055
410.00	0.2470	0.4487	1.245	1.044	0.087	395.75	0.9351	0.9523	1.014	1.585	0.043
409.28	0.2655	0.4705	1.237	1.048	0.091	395.70	0.9583	0.9664	1.005	1.744	0.028
409.04	0.2776	0.4852	1.227	1.044	0.088	395.57	0.9900	0.9902	1.001	2.142	0.008
407.78	0.3066	0.5162	1.220	1.058	0.100	395.55	1.0000	1.0000	1.000		0.000

Table 6 (Continued)

T/K	x_1	y_1	γ_1	γ_2	G^E_m/RT
Propyl Butanoate (1) + Heptane (2)					
371.49	0.0000	0.0000		1.000	0.000
371.59	0.0156	0.0099	2.555	0.996	0.011
372.02	0.0412	0.0182	1.736	1.000	0.022
372.55	0.0738	0.0293	1.528	1.008	0.039
373.52	0.1158	0.0443	1.426	1.012	0.051
374.58	0.1704	0.0628	1.322	1.027	0.070
376.05	0.2299	0.0858	1.273	1.037	0.083
377.12	0.2688	0.1022	1.251	1.041	0.090
378.18	0.3084	0.1180	1.213	1.051	0.094
378.82	0.3264	0.1272	1.209	1.050	0.095
379.26	0.3434	0.1347	1.199	1.055	0.098
380.40	0.3766	0.1517	1.185	1.057	0.099
381.10	0.4013	0.1631	1.168	1.066	0.101
381.73	0.4197	0.1733	1.162	1.069	0.102
382.76	0.4477	0.1896	1.152	1.072	0.102
383.58	0.4731	0.2025	1.134	1.082	0.101
384.37	0.4967	0.2157	1.121	1.092	0.101
385.17	0.5211	0.2300	1.110	1.104	0.102
386.33	0.5489	0.2503	1.104	1.108	0.101
387.45	0.5752	0.2692	1.093	1.115	0.097
388.53	0.6034	0.2901	1.085	1.129	0.097
389.93	0.6347	0.3150	1.071	1.142	0.092
392.28	0.6773	0.3581	1.060	1.144	0.083
393.86	0.7087	0.3887	1.047	1.161	0.076
395.82	0.7447	0.4299	1.038	1.179	0.070
398.78	0.7927	0.4976	1.033	1.194	0.062
401.76	0.8367	0.5675	1.022	1.219	0.050
404.36	0.8719	0.6377	1.021	1.227	0.045
407.82	0.9142	0.7319	1.013	1.257	0.031
410.00	0.9379	0.7942	1.008	1.271	0.022
411.74	0.9557	0.8453	1.003	1.291	0.014
413.35	0.9721	0.8973	1.002	1.316	0.009
414.57	0.9842	0.9383	1.001	1.362	0.006
415.39	0.9924	0.9696	1.003	1.372	0.006
416.41	1.0000	1.0000	1.000		0.000
Propyl Butanoate (1) + Nonane (2)					
423.53	1.0000	1.0000		1.000	0.000
422.70	0.0159	0.0410	2.187	0.995	0.008
422.17	0.0315	0.0657	1.794	0.998	0.017
421.65	0.0501	0.0916	1.594	1.003	0.026
420.47	0.1010	0.1581	1.408	1.012	0.045
420.00	0.1249	0.1871	1.364	1.016	0.052
419.47	0.1514	0.2175	1.326	1.022	0.061
418.87	0.1826	0.2505	1.286	1.032	0.072
417.50	0.2748	0.3435	1.215	1.056	0.093
416.51	0.3558	0.4186	1.174	1.081	0.107
416.24	0.3887	0.4472	1.156	1.091	0.109
415.76	0.4308	0.4802	1.134	1.115	0.116
415.39	0.4716	0.5162	1.125	1.130	0.120
415.21	0.5045	0.5416	1.108	1.147	0.120
414.90	0.5388	0.5707	1.103	1.163	0.122
414.80	0.5567	0.5808	1.089	1.185	0.123
414.65	0.5967	0.6185	1.086	1.190	0.120
414.47	0.6423	0.6568	1.077	1.213	0.117
414.35	0.6885	0.6929	1.063	1.251	0.112
414.40	0.7257	0.7260	1.055	1.266	0.104
414.45	0.7705	0.7645	1.045	1.299	0.094
414.55	0.8023	0.7921	1.037	1.328	0.085
414.65	0.8234	0.8113	1.032	1.346	0.079
414.76	0.8570	0.8421	1.026	1.387	0.069
414.95	0.8812	0.8648	1.020	1.422	0.059
415.06	0.9039	0.8884	1.018	1.447	0.052
415.26	0.9266	0.9123	1.015	1.481	0.042
415.35	0.9448	0.9311	1.013	1.544	0.036
415.64	0.9614	0.9509	1.009	1.560	0.026
415.69	0.9701	0.9614	1.009	1.585	0.023
415.89	0.9868	0.9807	1.007	1.793	0.014
416.00	0.9926	0.9891	1.007	1.794	0.011
416.41	1.0000	1.0000	1.000		0.000

7, 9) (2)}. Those values were then used to calculate the activity coefficients for the components in the liquid phase, taking the vapor phase to be nonideal, using the equation

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

with $\delta_{ji} = 2B_{ji} - B_{ii} - B_{jj}$ and where the second virial coefficients B_{ij} for the pure components and the mixtures were calculated using the correlations put forward by Tsonopoulos.[25] The molar volumes, V_i°, for pure component i at each equilibrium temperature were calculated using Rackett's equation as modified by Spencer and Danner[26] with the coefficients for the parameter Z_{RA} as published by Reid et al.[23] or calculated using the V_i° versus T values published in TRC d-5030.[10] The activity coefficient values calculated using eq 3 made it possible to determine the nondimensional Gibbs function G^E_m/RT. Table 6 presents all these results for each of the binary systems. The consistency test proposed by Fredenslund et al.[27] was applied to all the binary systems to observe the discrepancies between the experimental molar fraction in the vapor phase and that calculated by the model for each equilibrium state. The results presented in Table 6 were shown to be acceptable in that, for each system overall, the condition $\bar{\delta} = \sum_i (y_{i,\mathrm{exp}} - y_{i,\mathrm{cal}})/N \leq 0.01$ was fulfilled. Parts a and b of Figure 3 graphically represent the quantities $(y_1 - x_1)$ on x_1 for, respectively, the propyl ester + heptane and propyl ester + nonane systems. The plots also show the curves used to correlate the data, similar to eq 1 but with the first term replaced by $(y_1 - x_1)$. As stated in the Introduction, the literature does not contain VLE values for the systems considered in this study for purposes of comparison. Using the correlations already referred to above, the location of the azeotropic points for the mixtures was determined subject to the conditions $(y_1 - x_1) = 0$ and $(\mathrm{d}T/\mathrm{d}x)_p = 0$. The calculations showed that the system composed of propyl ethanoate + heptane had an azeotrope at $x_{az} = 0.423$ and $T_{az} = 366.9$ K, consistent with the values of (0.4215, 366.75) obtained at a pressure of 101.38 kPa and reported by Gmehling and Bölts.[4] The values for propyl butanoate + nonane were $x_{az} = 0.726$ and $T_{az} = 414.4$ K, but no literature values were found for comparison. These azeotropic points have also been depicted on the reduced coordinates in Figure 2, taking the geometric means of the critical properties of the pure components as the mixing rule for calculating the pseudocritical quantities. In conjunction with the other values for propyl ethanoate + heptane published by Gmehling and Bölts,[4] this enabled us to obtain an azeotropic line for that mixture. The azeotropic values and the corresponding quasi-parallel regression line for the system of ethyl ethanoate + heptane from Gmehling et al.[21] have likewise been drawn in. The box inset in Figure 2 contains the representation of the azeotropes and azeotropic line as a function of concentration at the singular point.

Processing of the VLE Data. The sets of isobaric VLE values presented for each of the mixtures considered in Table 6 were used as inputs to a correlation procedure taking a modified version of eq 1 as the basic equation, with the coefficient, A_i, values being treated as tempera-

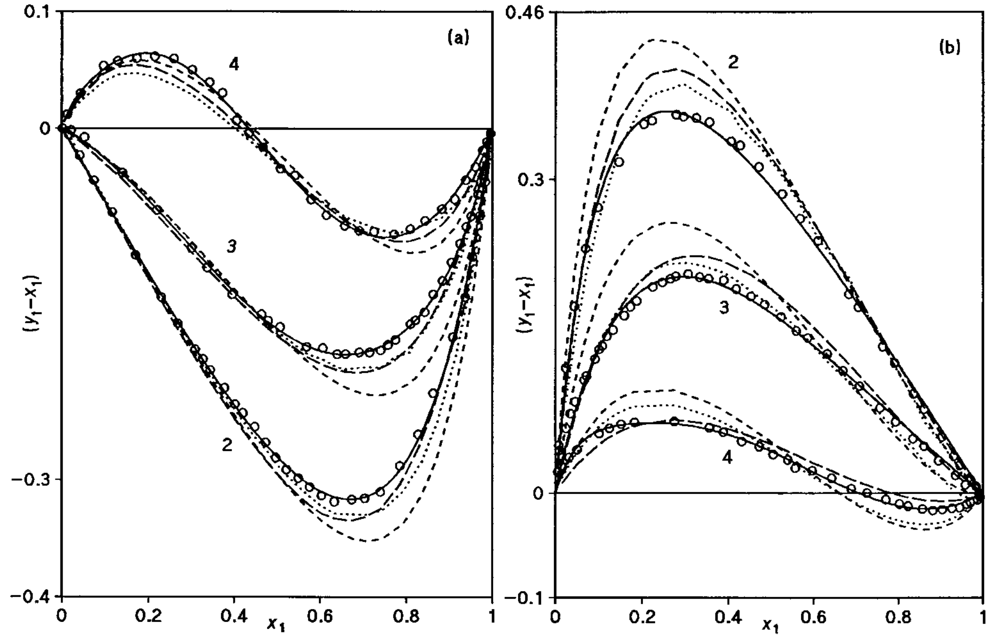

Figure 3. Representation of experimental values (○) and fitting curves for $(y_1 - x_1)$ versus x_1 for the mixtures propyl esters + n-alkanes: (a) VLE values for $H_{2u-1}C_{u-1}COO(CH_2)_2CH_3 + C_7H_{16}$; (b) VLE values for $H_{2u-1}C_{u-1}COO(CH_2)_2CH_3 + C_9H_{20}$. Labels indicate the u-values, and the dashed lines correspond to the following theoretical models: (— — —) UNIFAC by Gmehling et al.;[6] (- - -) ASOG by Tochigi et al.;[7] (· · ·) Nitta et al.[8]

ture-dependent. In summary, the set of equations used was as follows:

$$G^{E}_{m}/RT = q^{g} = x_1x_2[(A_{01}/T + A_{02}) + (A_{11}/T + A_{12})z] \quad \text{where} \quad z = x_1/(x_1 + k_g x_2) \tag{4}$$

$$H^{E}_{m}/(RTx_1x_2) = q^{h}/x_1x_2 = \sum A^{1}_{i} z^{i} \quad \text{where} \quad z = x_1/(x_1 + k_h x_2) \tag{5}$$

but since $H^{E}_{m} = [\partial(G^{E}_{m}/T)/\partial(1/T)]_{p,x}$, hence,

$$\text{the coefficients } A_{i1} = A^{1}_{i}T \tag{6}$$

The objective function (OF) for the calculation procedure was

$$\mathrm{OF} = \sum_{i=1}^{N}\left[\sum_{j=1}^{2}\frac{|(q^{\gamma}_{i,\mathrm{cal}} - q^{\gamma}_{i,\mathrm{exp}})|}{\sigma_{\gamma}} + \frac{|q^{g}_{i,\mathrm{cal}} - q^{g}_{i,\mathrm{exp}}|}{\sigma_{g}} + \frac{|q^{h}_{i,\mathrm{cal}} - q^{h}_{i,\mathrm{exp}}|}{\sigma_{h}}\right] \tag{7}$$

where $q^{\gamma} = \gamma_j$, $q^{g} = G^{E}_{m}/RT$, and $q^{h} = H^{E}_{m}/RT$. The values of σ were the allowable or acceptable deviations for each of the respective quantities in the numerators of eq 7. In the procedure, for each concentration the correlations of the enthalpies were used, with the coefficient A^{1}_{i} values from Table 3, to fit the nondimensional Gibbs function and the activity coefficient values shown in Table 6. The correlations calculated were generally acceptable, as shown by the curves for G^{E}_{m}/RT and γ_j, on x_1 plotted with solid lines in Figure 4. The reproductions of the curves were acceptable for all the systems considered. Table 7 presents the optimum values for the coefficients $A_{0,i}$ in eq 4 and the standard deviations for each of the quantities processed using the algorithm employed, the Solver computational subroutine from the Excel spreadsheet, version 5.0a, from Microsoft. The errors for the final excess enthalpy, H^{E}_{m}, estimates were good, being less than 2% in all cases.

Table 7. Fitting Coefficients for Eq 4 Obtained Correlating the Quantities $q^{g} = G^{E}_{m}/RT$, $q^{h} = H^{E}_{m}/RT$, and $q^{\gamma} = \gamma_i$ as a Function of Ester Mole Fraction, and the Corresponding Standard Deviations $s(q^{\gamma})$, $s(q^{g})$, and $s(q^{h})$ for Binary Mixtures of Propyl Alkanoate (1) + n-Alkane (2)

mixture	coefficients	$s(q^{\gamma})$	$s(q^{g})$	$s(q^{h})$
	Propyl Ethanoate (1) + Heptane (2)			
$k_g = 0.20$[a]	$A_{01} = 709.33$ $A_{02} = -173.26$ $A_{11} = -1.119$ $A_{12} = 0.329$	0.036	0.007	0.02
	Propyl Ethanoate (1) + Nonane (2)			
$k_g = 0.02$[a]	$A_{01} = 1012.64$ $A_{02} = -377.75$ $A_{11} = -1.755$ $A_{12} = 0.724$	0.154	0.005	0.01
	Propyl Propanoate (1) + Heptane (2)			
$k_g = 0.12$[a]	$A_{01} = 533.09$ $A_{02} = -120.24$ $A_{11} = -0.703$ $A_{12} = 0.079$	0.032	0.007	0.02
	Propyl Propanoate (1) + Nonane (2)			
$k_g = 0.03$[a]	$A_{01} = 568.62$ $A_{02} = -86.01$ $A_{11} = -0.157$ $A_{12} = -0.560$	0.085	0.010	0.02
	Propyl Butanoate (1) + Heptane (2)			
$k_g = 0.03$[a]	$A_{01} = 465.04$ $A_{02} = -124.84$ $A_{11} = 0.307$ $A_{12} = -0.822$	0.025	0.005	0.01
	Propyl Butanoate (1) + Nonane (2)			
$k_g = 1.32$[a]	$A_{01} = 477.26$ $A_{02} = -231.76$ $A_{11} = -0.647$ $A_{12} = 0.510$	0.089	0.005	0.01

[a] Obtained by fit.

Theoretical VLE Modeling. Theoretical estimates of the isobaric VLE values at 101.32 kPa were calculated for all six mixtures of a propyl ester (1) + an n-alkane (2) using various models already published in the specialized literature. These models have been applied and tested in our studies, with a view to updating them as appropriate, and were the ASOG model using the parameters proposed by Tochigi et al.;[7] the original version of the UNIFAC model of Fredenslund et al.[27] using the parameters published by Hansen et al.;[5] and the version of that same model prepared by Gmehling et al.,[6] which also allowed estimation of the enthalpies for the systems under consideration. In addition, the model of Nitta et al.[8] using the set of

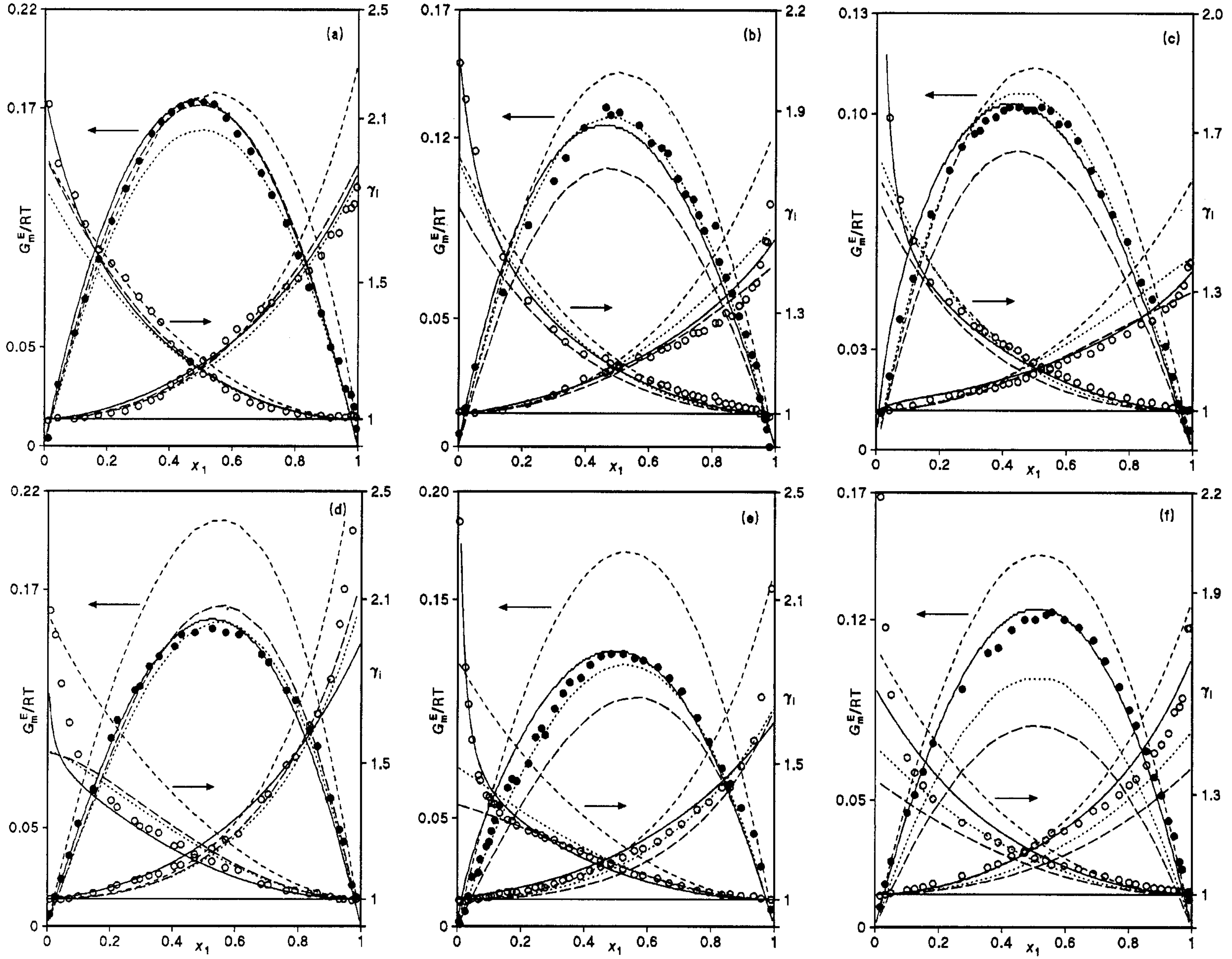

Figure 4. Experimental VLE values, fitting curves, and theoretical predictions of G_m^E/RT (●) and γ_i (○) versus x_1 for the binary mixtures (x)propyl esters (1) + (1 − x)n-alkane (2). Parts a, b, and c correspond, respectively, to propyl ethanoate, or propyl propanoate, or propyl butanoate + heptane; parts d, e, and f correspond, respectively, to propyl ethanoate, or propyl propanoate, or propyl butanoate + nonane: (—) eq 4; (— — —) UNIFAC by Gmehling et al.;[6] (- - -) ASOG by Tochigi et al.;[7] (· · ·) Nitta et al.[8]

parameter values reported by Ortega and Legido[28] was employed here to estimate the thermodynamic quantities, H_m^E and V_m^E, for the ester + *n*-alkane mixtures, even though it has not customarily been used by our team for isobaric VLE data.

The ASOG model did not yield good predictions of the characteristic isobaric VLE values for the mixtures considered but rather resulted in appreciable discrepancies for the activity coefficient values and the Gibbs function. The predictions were in all cases higher than the experimental values, and the differences increased distinctly with hydrocarbon chain length (Figure 4). The concentration estimates were likewise not very good (Figure 3). The poorest estimates of the VLE values were obtained using the UNIFAC model with the parameter values from Hansen et al.,[5] and the corresponding plots have therefore not been included in Figures 3 and 4. On the other hand, the version of the UNIFAC model proposed by Gmehling et al.[6] yielded good predictions for the mixtures that contained ethanoates, with differences of around 5% for the γ_i, values, though the differences tended to increase with propyl ester chain length, yielding estimates for the Gibbs function and the γ_i values that were lower than the experimental values (Figure 4). Using the same set of parameters, that model was also used to estimate the excess enthalpies. The inset in Figure 1 reveals acceptable estimates of the H_m^E values for the mixtures containing propyl ethanoate, with differences <5%. For the mixtures that contained propanoate and butanoate the predictions were lower than the experimental H_m^E values, even though the overall differences can be considered quantitatively acceptable at <10%. Finally, as shown in Figure 4f, the model of Nitta et al.[8] yielded excellent predictions of the isobaric VLE values for all the mixtures studied here except propyl butanoate + nonane. Considering the difficulties intrinsic to the model, the H_m^E and V_m^E estimates were acceptable. The predicted values for those quantities were lower than the experimental values for the nonethanoate-containing mixtures and higher for the propyl ethanoate-containing mixtures. The estimates of the concentration values obtained using the model of Nitta et al.[8] were acceptable.

Summing up, applying the theoretical models to the propyl ester + *n*-alkane systems considered here resulted in the gradual failure of the models as the chain length of the mixture components increased.

Literature Cited

(1) Galván, S.; Ortega, J.; Susial, P.; Peña, J. A. Isobaric Vapor-Liquid Equilibria for Propyl Methanoate + (*n*-Alkanes, C_7, C_8, C_9) or *n*-Alkanols (C_2, C_3, C_4). *J. Chem. Eng. Jpn.* **1994**, *27* (4), 529−534.

(2) Gmehling, J.; Onken, U.; Arlt, W.; Grenzheuser, P.; Rarey, J.; Weidlich, U. *Vapor-Liquid Equilibrium Data Collection;* DECHEMA Chemistry Data Series 1; DECHEMA: Frankfurt, 1977; Parts 1 to 8.

(3) Slavin, A. A.; Abramzon, A. A. Vapor-liquid equilibrium data at ambient conditions in the systems esters-complex solvents. *Zh. Prikl. Khim.* (*Leningrad*) **1977**, *50*, 773−777.

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

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

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

(7) Tochigi, K. D.; Tiegs, D.; Gmehling, J.; Kojima, K. Determination of new ASOG Parameters. *J. Chem. Eng. Jpn.* **1990**, *23*, 453−463.

(8) Nitta, T.; Turek, E. A.; Greenkorn, R. A.; Chao, K. C. A group contribution molecular model of liquids and solutions. *AIChE J.* **1977**, *23*, 144−160.

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

(10) *TRC Thermodynamics Tables Non-Hydrocarbons*; Thermodynamic Research Center: Texas A&M University System, College Station, TX, extant 1998; a-5000 1993; a-5030 1967; d-5030 1966; k-5030 1965.

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

(12) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1965; Vol. 2.

(13) Ortega, J.; Peña, J.; de Afonso, C. Isobaric vapor-liquid equilibria of ethyl acetate + ethanol mixtures at 760 ± 0.5 mmHg. *J. Chem. Eng. Data* **1986**, *31*, 339−341.

(14) Ortega, J.; Vidal, M.; Toledo-Marante, F. J.; Plácido, J. Thermodynamic properties of (a propyl ester+an *n*-alkane). XII Excess molar enthalpies and volumes. *J. Chem. Thermodyn.*, **1999**, *31*, 1025−1044.

(15) Ortega, J.; Alcalde, R. Determination and Algebraic Representation of Volumes of Mixing at 298.15 K of Methyl *n*-Alkanoates (from Ethanoate to *n*-Pentadecanoate) with *n*-Pentadecane. *Fluid Phase Equilib.* **1992**, *71*, 49−62.

(16) Dusart, O.; Piekarski, C.; Piekarski, S.; Viallard, A. Excess volumes of binary mixtures *n*-heptane+esters and *n*-heptane+cetone. *J. Chim. Phys.* **1976**, *78*, 837−844.

(17) Lorenzana, T.; Legido, J. L.; Jiménez, E.; Fernández, J.; Pias, L.; Ortega, J.; Paz, M. I. Thermodynamic properties of (a propyl ester+*n*-alkane) at 298.15 K. I. *J. Chem. Thermodyn.* **1989**, *21*, 1017−1022.

(18) Lorenzana, T.; Legido, J. L.; Jiménez, E.; Fernández, J.; Pias, L.; Ortega, J.; Paz, M. I. Thermodynamic properties of (a propyl ester+*n*-alkane) at 298.15 K. II. *J. Chem. Thermodyn.* **1990**, *22*, 263−268.

(19) Ortega, J.; Plácido, J.; Toledo, F.; Vidal, M.; Siimer, E.; Legido, J. L. Behaviour of binary mixtures of an alkyl methanoate+an *n*-alkane. New experimental values and an interpretation using the UNIFAC model. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2967−2974.

(20) González, C.; Ortega, J.; Hernández, P.; Galván, S. Experimental Determination of Densities and Isobaric Vapor-Liquid Equilibria of Binary Mixtures Formed by a Propyl Alkanoate (Methanoate to Butanoate) + An Alkan-2-ol (C_3, C_4). *J. Chem. Eng. Data* **1999**, *44*, 772−783.

(21) Gmehling, J.; Menke, J.; Krafczyk, J.; Fisher, K. *Azeotropic Data*; VCH: Weinheim, 1994.

(22) Boublik, T.; Fried, V.; Hála, E. *The Vapour Pressures of Pure Substances*; Elsevier: Amsterdam, 1973.

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

(24) Ortega, J.; González, C.; Peña, J.; Galván, S. Thermodynamic study on binary mixtures of propyl ethanoate and an alkan-1-ol (C2−C4). Isobaric vapor-liquid equilibria and excess properties. *Fluid Phase Equilib.* **2000**, *170*, 87−111.

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

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

(27) Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC. A Group Contribution Model*; Elsevier: Amsterdam, 1977; pp 27−64.

(28) Ortega, J.; Legido, J. L. Application of the UNIFAC and Nitta models to describing the behavior of methyl ester/alkane mixtures, and experimental data for (methyl *n*-alkanoates+*n*-heptadecane) binary mixtures. *Fluid Phase Equilib.* **1994**, *95*, 175−214.

Received for review November 14, 2000. Accepted April 17, 2001.

JE000358A