

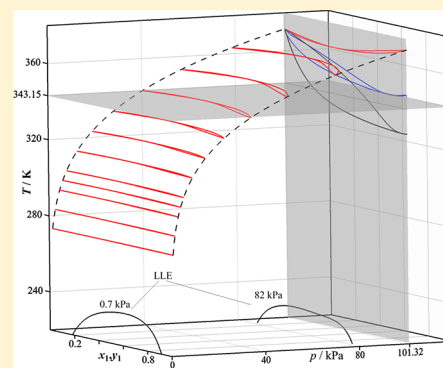
# Multiproperty Correlation of Experimental Data of the Binaries Propyl Ethanoate + Alkanes (Pentane to Decane). New Experimental Information for Vapor–Liquid Equilibrium and Mixing Properties

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**ABSTRACT:** A thermodynamic study is carried out on binary systems composed of propyl ethanoate with six alkanes, from pentane to decane. Vapor pressures of the ester and the isobaric vapor–liquid equilibria of these six mixtures were measured at 101.32 kPa in a small-capacity ebulliometer and also the mixing properties  $y^E = v^E, h^E$  over a range of temperatures and at atmospheric pressure. Adequate correlations are drawn for the surfaces  $y^E = y^E(x, T)$  with an interpretation on the behavior of the mixtures and also using  $c_p^E$  data from literature. The mixing processes are all endothermic with a change in the slope direction of the function  $h^E = h^E(T)$  for the binary systems, which all present expansive effects, with  $v^E > 0$  and also  $(\partial v^E / \partial T)_p > 0$ . The results of the different properties are analyzed within a general context of the behavior of ester + alkane systems. A parametric model is used that enables the simultaneous correlation of the experimental values of different thermodynamic properties for each of the systems considered, slightly improving on the representation obtained with the nonrandom two-liquid (NRTL) model. The representation of vapor–liquid equilibrium (VLE) and  $h^E$  properties with the universal functional activity coefficient (UNIFAC) group contribution model is acceptable, although it does not reflect the change in enthalpies with varying temperature, resulting in an unacceptable estimation of  $c_p^E$ .



## INTRODUCTION

This work follows on from previous studies<sup>1–5</sup> carried out by our research group that form part of a line of investigation aimed at studying the behavior in solution of systems of alkyl esters with alkanes. It is important to contribute new experimental data which, in addition to the above, enable knowledge of the capacity of the model to represent several of the systems' properties. In this line, studies on methyl<sup>1</sup> and ethyl<sup>2,3</sup> ethanoates have been published, and in this work the properties of mixtures of propyl ethanoate with six alkanes, from pentane to decane, are presented. Specifically, excess properties have been measured at different temperatures, of  $v^E$  at (291.15, 298.15, 318.15, and 328.15) K,  $h^E$  at (291.15, 298.15, and 318.15) K, and isobaric vapor–liquid equilibria (VLE) at 101.32 kPa. In previous works, measurements of  $v^E$  and  $h^E$  were made with odd alkanes<sup>4,5</sup> at two of the indicated temperatures, 298 K and 318 K; isobaric VLE data of propyl ethanoate + (C<sub>7</sub>, C<sub>8</sub>) have also been published previously.<sup>6</sup> All of these data will help to verify the behavior and gain a greater understanding of these solutions.

Other investigators have also worked with these systems, and there are considerable  $v^E$  data published at 298.15 K,<sup>7–11</sup> but only one study<sup>7</sup> exists concerning the effect of temperature on this property.  $h^E$  values for mixtures with  $n = 6, 7$ , and  $8$  in the set represented by H<sub>3</sub>CCOOC<sub>3</sub>H<sub>7</sub> (1) + C<sub>n</sub>H<sub>2n+2</sub> (2) have also been published.<sup>11–13</sup> However, the bibliographic information on VLE is very limited, since only data for isothermic VLE<sup>13</sup> have been found for the binary system with  $n = 7$  measured at 11 temperatures in the

interval 273 K to 363 K. Values of  $g^E$  by chromatography have even been published at 298.15 K,<sup>14</sup> for the binaries of the same ester with saturated hydrocarbons of  $n = 6$  and  $7$ . Finally, values of  $c_p^{E9}$  are presented for systems with  $n = 7$  and  $10$ . All of those data are used for comparison with the experimental results obtained here, when pertinent, incorporating in the database constructed for the purpose of performing a multiproperty correlation process that uses all of the experimental data available. A model and a procedure designed by our team, used in previous works,<sup>15,16</sup> is used. The same procedure is employed with the NRTL model.<sup>17</sup>

The experimental information obtained is used here to confirm the efficacy of the UNIFAC group contribution method<sup>18</sup> and to check the representation capacity of that model when the specific interaction parameters COOC/CH<sub>2</sub> are used for ethanoates.

## EXPERIMENTAL SECTION

**Materials.** The propyl ethanoate and hydrocarbons were of the highest commercial purity (> 0.99 w/w) and supplied by Aldrich. However, before use they were degasified with ultrasound for several hours and stored in the dark over a molecular sieve (Fluka 0.3 nm) to eliminate traces of water, and the final purity of the products was verified by gas chromatography (GC).

Received: November 8, 2012

Accepted: January 16, 2013

Published: February 7, 2013

Table 1. Properties of Pure Compounds<sup>a</sup>. Densities and Refractive Indices Were Measured at Atmospheric Pressure

compound	supplier/purity (% mass)	$T_b^{\circ}/\text{K}$		$T/\text{K}$	$\rho/\text{kg}\cdot\text{m}^{-3}$		$n_D$		
		exp.	lit.		exp.	lit.	exp.	lit.	
propyl ethanoate	Aldrich/99 %	374.34	374.55 <sup>c</sup> 374.69 <sup>g</sup>	291.15→	889.58				
				298.15→	882.55	882.55 <sup>b,c</sup> 883.03 <sup>g</sup>	1.3818	1.3816 <sup>b,c</sup>	
				318.15→	859.78	859.78 <sup>d</sup>	1.3720	1.3721 <sup>d</sup>	
				328.15→	848.30				
pentane	Aldrich/> 99 %	309.30	309.30 <sup>e</sup> 309.22 <sup>g</sup>	291.15→	628.19				
				298.15→	621.35	621.35 <sup>e</sup> 621.39 <sup>g</sup>	1.3545	1.3545 <sup>e</sup> 1.35472 <sup>g</sup>	
hexane	AlfaAesar/99 %	341.88	341.88 <sup>e</sup> 341.89 <sup>g</sup>	291.15→	661.11				
				298.15→	654.84	654.84 <sup>e</sup> 654.81 <sup>g</sup>	1.3723	1.3722 <sup>e</sup> 1.37226 <sup>g</sup>	
				318.15→	636.60	636.67 <sup>f</sup>	1.3615	1.3615 <sup>f</sup>	
				328.15→	627.21				
heptane	Aldrich/> 99 %	371.56	371.49 <sup>c</sup> 371.58 <sup>g</sup>	291.15→	685.28				
				298.15→	679.48	679.27 <sup>c</sup> 679.51 <sup>g</sup>	1.3852	1.3851 <sup>c</sup> 1.38511 <sup>g</sup>	
				318.15→	662.06	662.04 <sup>d</sup> 662.32 <sup>f</sup>	1.3748	1.3748 <sup>d</sup> 1.3750 <sup>f</sup>	
				328.15→	653.72				
octane	Aldrich/> 99 %	398.83	398.83 <sup>e</sup> 398.82 <sup>g</sup>	291.15→	704.13				
				298.15→	698.60	698.60 <sup>e</sup> 698.49 <sup>g</sup>	1.3952	1.3952 <sup>e</sup> 1.39505 <sup>g</sup>	
				318.15→	682.17	682.09 <sup>f</sup>	1.3855	1.3855 <sup>f</sup>	
				328.15→	674.14				
nonane	Aldrich/> 99 %	423.94	423.53 <sup>c</sup> 423.95 <sup>g</sup>	291.15→	719.20				
				298.15→	713.85	713.85 <sup>c</sup> 713.81 <sup>g</sup>	1.4031	1.4030 <sup>c</sup> 1.40311 <sup>g</sup>	
				318.15→	698.06	698.06 <sup>d,f</sup>	1.3938	1.3939 <sup>e,f</sup>	
				328.15→	690.17				
decane	Aldrich/> 99 %	447.30	447.30 <sup>e</sup> 447.27 <sup>g</sup>	291.15→	731.22				
				298.15→	726.20	726.20 <sup>e</sup> 726.25 <sup>g</sup>	1.4096	1.4096 <sup>e</sup> 1.40967 <sup>g</sup>	
				318.15→	710.90	711.43 <sup>f</sup>	1.4008	1.4008 <sup>f</sup>	
				328.15→	703.34				

<sup>a</sup>Uncertainties  $u$  are:  $u(T) = \pm 0.02$  K,  $u(n) = \pm 0.0002$ , and  $u(\rho) = \pm 0.02$  kg·m<sup>-3</sup>. <sup>b</sup>Reference 4. <sup>c</sup>Reference 6. <sup>d</sup>Reference 5. <sup>e</sup>Reference 3. <sup>f</sup>Reference 19. <sup>g</sup>Reference 20.

The quality of the pure compounds was then confirmed by measuring a series of physical properties such as the density  $\rho$  and the refractive index  $n_D$ , at different temperatures, and the normal boiling temperature  $T_{b,i}$ . Table 1 indicates the manufacturer of each compound and the values measured for different properties. In general, the comparison between our values and those found in the literature can be considered acceptable.

**Apparatus and Procedures.** An Anton Paar DMA-60/602 digital densimeter, with a reading error of  $\pm 0.02$  kg·m<sup>-3</sup> was used to measure the densities of pure compounds  $\rho_i$  and of the mixtures  $\rho$ . Mixtures ( $x \pm 0.0002$ ) were prepared synthetically by mass on a AND balance, model ER182A, with an accuracy of  $\pm 1 \cdot 10^{-5}$  g to obtain the curves of  $\rho = \rho(x)$  at different temperatures in the interval 291.15 K to 328.15 K. In the densimeter the temperature was controlled by circulating water using a CB7 Hetobirkeroad thermostatic bath, with a control of ( $T \pm 0.01$ ) K. Pairs of values ( $x, \rho$ ), obtained at a temperature of 298.15 K for the binaries:  $\{x_1\text{H}_3\text{CCO}_2\text{C}_3\text{H}_7$  (1) +  $x_2\text{C}_n\text{H}_{2n+2}$  (2) ( $n = 5$  to 10)) were used to define the following equation

$$\rho = \rho_1 x_1 + \rho_2 x_2 + x_1 x_2 (a_0 + a_1 x_1 + a_2 x_1^2) \quad (1)$$

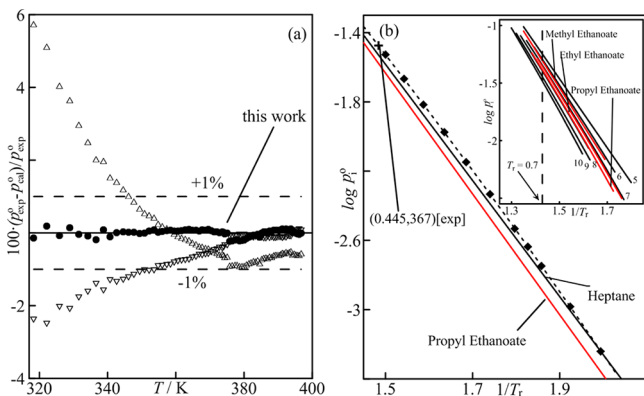
This expression was used to obtain the compositions  $x_i$  and  $y_i$  of the phase equilibria after measuring, respectively, the densities of the samples of liquid and vapor phases. The  $a_i$  parameters are obtained by a least-squares procedure with an excellent goodness of fit ( $r^2 \gg 0.999$ ) and are collected in Table 2. Values of  $x_1, \rho, \rho_1,$

Table 2. Parameters  $a_i$  Obtained for eq 1 Correlating the Density–Composition Values Measured at 298.15 K and Atmospheric Pressure, and Standard Deviations  $s(\rho)$ , for Each of the Mixtures

propyl ethanoate +	$a_1$	$a_2$	$a_3$	$s(\rho)/\text{kg}\cdot\text{m}^{-3}$
pentane	-15.526	29.648	-15.466	0.08
hexane	-45.413	0.679	-1.554	0.05
heptane	-61.727	-7.089	-10.146	0.06
octane	-73.975	-7.411	-22.361	0.06
nonane	-80.556	-8.831	-36.504	0.07
decane	-85.824	-4.782	-56.468	0.05

and  $\rho_2$ , are, respectively, the ester composition, the density of the mixture, and the densities of the pure components and are also used to calculate the excess volumes  $v^E$ , for which the uncertainty was estimated to be  $\pm 2 \cdot 10^{-9}$  m<sup>3</sup>·mol<sup>-1</sup>.

Vapor pressures of the pure compounds and the vapor–liquid equilibria were determined experimentally with a



**Figure 1.** (a) Percentage between experimental vapor pressures obtained in this work (●) for propyl ethanoate and those from ref 27 (Δ) and ref 30 (▽). (b) +, experimental azeotropic point ( $x_{az}$ ,  $T_{az}$ ); and vapor pressures lines in reduced coordinates for propyl ethanoate (this work) and heptane, ref 3, azeotropic points (◆) from ref 13, for binary { $x$  propyl ethanoate +  $(1-x)$  heptane}, and azeotropic-line (---) obtained by correlation:  $\log p_{r,aze}^o = 2.6496 - 2.3743/(T_{r,aze} - 0.0983)$ . Inset shows the vapor pressure lines for the three first alkyl ethanoates and those alkanes studied; numbers indicate the number of carbon atoms in the saturated hydrocarbon.

small-capacity system through which both phases recirculated; the operational procedure has been described previously.<sup>21–23</sup>

The system reached the equilibrium when the temperature remained constant within the experimental uncertainty ( $T \pm 0.01$ ) K at the working pressure  $p = 101.32$  kPa, for at least fifteen minutes. Then, samples of both phases are extracted and their densities measured; regression of eq 1 obtains optimum values for the compositions of the liquid phases  $x_i$  and vapor phases  $y_i$  with an uncertainty of  $\pm 0.0007$ . The pressure was measured with a PPC2 controller/calibrator instrument, which stabilizes the still at  $(101.32 \pm 0.02)$  kPa. The temperature was obtained by direct reading at two Pt-100 thermoresistances, calibrated according to ITS90, introduced in the ebulliometer (see ref 21) connected to a Comark 6800 digital apparatus that gives a reading of  $(T \pm 0.01)$  K.

The mixing enthalpies  $h^E$  were measured with a MS80D Calvet conduction calorimeter by Setaram, calibrated as described in a previous work.<sup>24</sup> Thermograms obtained in the experimentation were processed with the Setsoft software supplied by the manufacturer. The temperature of the sample was confirmed by introducing a PT100 sensor, connected to a digital thermometer by ASL, into the calorimetric cells containing paraffin oil. Then the controller was adjusted to ensure the temperature of the sample within the interval  $(T \pm 0.002)$  K. Correct functioning of the system was verified by reproducing the  $h^E$  of known systems<sup>25,26</sup> at the temperatures of 298.15 K and 318.15 K, since

**Table 3.** Vapor Pressures for Propyl Ethanoate<sup>a</sup>

$T/K$	$p_i^o/kPa$	$T/K$	$p_i^o/kPa$	$T/K$	$p_i^o/kPa$	$T/K$	$p_i^o/kPa$
318.35	12.14	358.41	60.24	375.78	106.19	388.63	154.37
322.19	14.43	359.52	62.59	376.51	108.56	389.16	156.68
325.87	17.04	360.63	65.00	377.29	111.14	389.68	158.99
328.95	19.43	361.71	67.41	377.98	113.47	390.18	161.23
331.59	21.77	362.73	69.74	378.69	115.96	390.68	163.46
334.22	24.29	363.81	72.28	379.36	118.30	391.22	165.89
336.60	26.79	364.84	74.80	380.04	120.71	391.70	168.13
338.75	29.12	365.86	77.35	380.74	123.19	392.24	170.62
340.72	31.53	366.81	79.80	381.41	125.61	392.73	172.98
342.66	33.96	367.70	82.11	382.06	128.01	393.23	175.35
344.52	36.46	368.62	84.58	382.71	130.42	393.71	177.64
346.15	38.78	369.51	87.01	383.34	132.85	394.16	180.01
347.73	41.14	370.41	89.57	384.01	135.42	394.66	182.44
349.35	43.69	371.18	91.80	384.55	137.67	395.17	185.03
350.81	46.08	371.99	94.17	385.18	140.04	395.67	187.59
352.19	48.41	372.78	96.55	385.79	142.47	396.16	190.10
353.57	50.84	373.55	98.87	386.36	144.80	396.69	192.76
354.78	53.11	373.97	100.18	386.90	147.09		
356.03	55.48	374.52	101.32	387.49	149.51		
357.29	57.96	375.10	103.76	388.06	151.96		

<sup>a</sup>Uncertainties  $u$  are:  $u(T) = \pm 0.01$  K and  $u(p) = \pm 0.02$  kPa.

**Table 4.** Coefficients of Antoine Equation  $\log p_i^o/(kPa) = A - B/[T/(K) - C]$  and Acentric Factor  $\omega$  Calculated for Propyl Ethanoate

$A$ (a)	$B$ (b)	$C$ (c)	$\omega$	literature	$\Delta T/K$
6.05433	1221.75	72.56		this work	315 to 400
(2.53146)	(2.22402)	(0.1321)	0.385	this work	
6.51160	1524.56	36.19		27	320 to 430
(2.977)	(2.767)	(0.070)	0.415	27, 29	
6.07167	1240.55	69.104	0.384	30	
			0.387	31	

Table 5. Experimental Values of ( $x_1, \rho, v^E$ ) for Binary Systems  $\text{CH}_3\text{COO}(\text{CH}_2)_2\text{CH}_3$  (1) +  $\text{C}_n\text{H}_{2n+2}$  ( $n = 5$  to 10) (2) at Four Temperatures of (291.15, 298.15, 318.15, and 328.15) K and Atmospheric Pressure<sup>a</sup>

$x_1$	$\rho$ kg·m <sup>-3</sup>	$10^9 \cdot v^E$ m <sup>3</sup> ·mol <sup>-1</sup>	$x_1$	$\rho$ kg·m <sup>-3</sup>	$10^9 \cdot v^E$ m <sup>3</sup> ·mol <sup>-1</sup>	$x_1$	$\rho$ kg·m <sup>-3</sup>	$10^9 \cdot v^E$ m <sup>3</sup> ·mol <sup>-1</sup>
T = 291.15 K								
Propyl Ethanoate (1) + Pentane (2)								
0.0000	628.22	0	0.3338	714.10	216	0.7697	829.23	20
0.0121	631.16	40	0.3934	729.80	192	0.8277	844.59	-7
0.0427	638.75	113	0.4636	748.35	156	0.8911	861.27	-21
0.0780	647.67	165	0.5224	763.88	128	0.9230	869.65	-27
0.1417	663.97	220	0.5876	781.12	96	1.0000	889.58	0
0.2048	680.25	250	0.6565	799.31	68			
0.2734	698.21	238	0.7136	814.38	46			
Propyl Ethanoate (1) + Hexane (2)								
0.0000	661.17	0	0.3085	722.16	599	0.7020	812.34	435
0.0120	663.39	39	0.3804	737.74	607	0.7697	829.14	361
0.0372	667.96	141	0.4420	751.35	607	0.8208	842.17	285
0.0924	678.46	286	0.5117	767.18	578	0.8835	858.38	198
0.1648	692.70	423	0.5781	782.58	544	0.9247	869.25	134
0.2357	706.98	534	0.6400	797.33	488	1.0000	889.58	0
Propyl Ethanoate (1) + Heptane (2)								
0.0000	685.28	0	0.3308	738.58	703	0.7257	819.57	545
0.0086	686.58	17	0.3974	750.86	733	0.8000	837.21	438
0.0320	690.09	75	0.4644	763.73	741	0.8457	848.54	355
0.0864	698.20	247	0.5398	778.88	722	0.9057	864.03	222
0.1706	711.31	471	0.6055	792.76	669	0.9708	881.58	61
0.2573	725.67	628	0.6723	807.44	603	1.0000	889.58	0
Propyl Ethanoate (1) + Octane (2)								
0.0000	704.13	0	0.4206	762.45	862	0.8181	841.89	492
0.0120	705.67	9	0.4808	772.73	870	0.8638	853.08	385
0.0405	708.88	142	0.5357	782.59	857	0.9109	865.09	271
0.1465	721.91	496	0.6206	798.82	799	0.9798	883.92	54
0.1905	727.76	599	0.6668	808.14	758	1.0000	889.58	0
0.2679	738.63	738	0.7082	816.92	696			
0.3573	752.22	825	0.7644	829.30	610			
Propyl Ethanoate (1) + Nonane (2)								
0.0000	719.20	0	0.4338	770.86	904	0.7948	837.08	570
0.0569	724.61	232	0.4846	778.66	907	0.8162	841.91	528
0.1163	730.70	423	0.5686	792.44	892	0.8844	858.48	334
0.1916	739.04	611	0.6289	803.22	840	0.9349	871.71	169
0.2820	749.98	771	0.6876	814.43	770	0.9464	874.88	125
0.3583	760.02	866	0.7441	826.00	675	1.0000	889.58	0
Propyl Ethanoate (1) + Decane (2)								
0.0000	731.22	0	0.4514	778.28	957	0.8151	841.83	581
0.0491	735.16	192	0.5221	788.37	954	0.8554	851.23	458
0.1081	740.19	402	0.5892	798.75	934	0.8932	860.45	351
0.2054	749.44	651	0.6468	808.44	888	0.9454	874.25	165
0.2933	758.78	810	0.7079	819.64	804	0.9719	881.50	91
0.3720	767.96	918	0.7955	837.47	634	1.0000	889.58	0
T = 298.15 K								
Propyl Ethanoate (1) + Pentane								
0.0000	621.35	0	0.2830	693.62	246	0.6565	792.11	76
0.0101	623.70	52	0.3439	709.68	212	0.7085	805.89	48
0.0346	629.76	110	0.4072	726.35	183	0.8437	841.60	1
0.0754	640.01	176	0.4881	747.65	150	0.9205	861.84	-16
0.1377	655.88	236	0.5218	756.54	135	1.0000	882.54	0
0.1977	671.36	257	0.5968	776.36	99			
Propyl Ethanoate (1) + Hexane (2)								
0.0000	654.84	0	0.3539	724.89	691	0.7772	823.86	392
0.0175	658.01	68	0.4197	739.38	673	0.8357	838.87	292
0.0350	661.24	126	0.4795	752.70	667	0.8934	853.93	194
0.0831	670.27	268	0.5417	766.92	637	0.9187	860.54	162

Table 5. continued

$x_1$	$\rho$ kg·m <sup>-3</sup>	$10^3 \cdot v^E$ m <sup>3</sup> ·mol <sup>-1</sup>	$x_1$	$\rho$ kg·m <sup>-3</sup>	$10^3 \cdot v^E$ m <sup>3</sup> ·mol <sup>-1</sup>	$x_1$	$\rho$ kg·m <sup>-3</sup>	$10^3 \cdot v^E$ m <sup>3</sup> ·mol <sup>-1</sup>
Propyl Ethanoate (1) + Hexane (2)								
0.1535	683.94	419	0.6040	781.52	589	0.9749	875.68	52
0.2218	697.58	531	0.6583	794.45	546	1.0000	882.54	0
0.2836	710.25	607	0.7242	810.59	466			
Propyl Ethanoate (1) + Heptane (2)								
0.0000	679.48	0	0.3750	740.19	787	0.7930	828.44	505
0.0149	681.75	24	0.4386	752.12	806	0.8688	847.30	351
0.0308	684.03	84	0.5062	765.33	804	0.9100	858.00	252
0.0953	693.48	313	0.5643	777.16	780	0.9508	868.82	158
0.1680	704.76	503	0.6488	795.15	719	1.0000	882.54	0
0.2358	715.78	642	0.6684	799.45	702			
0.3084	728.21	739	0.7446	816.87	594			
Propyl Ethanoate (1) + Octane (2)								
0.0000	698.57	0	0.3895	751.12	903	0.8145	834.19	533
0.0149	700.30	51	0.4733	765.04	930	0.8620	845.60	435
0.0603	705.44	256	0.5382	776.56	917	0.9221	860.87	286
0.1039	710.78	389	0.5953	787.32	873	0.9349	864.32	240
0.2154	725.25	687	0.6543	798.99	814	1.0000	882.54	0
0.2536	730.62	749	0.7043	809.37	750			
0.3283	741.54	860	0.7628	822.24	641			
Propyl Ethanoate (1) + Nonane (2)								
0.0000	713.85	0	0.3636	754.58	964	0.7321	816.53	797
0.0361	717.15	167	0.4312	764.15	1005	0.7908	829.02	687
0.0384	717.37	175	0.5061	775.63	1005	0.8257	836.90	608
0.1106	724.51	441	0.5653	785.30	995	0.8918	852.78	436
0.2023	734.50	689	0.6308	796.89	934	0.9404	865.63	250
0.2833	744.19	846	0.6728	804.80	878	1.0000	882.54	0
Propyl Ethanoate (1) + Decane (2)								
0.0000	726.2	0	0.4509	772.01	1087	0.7988	830.87	784
0.0402	729.10	231	0.5172	781.22	1101	0.8462	841.53	644
0.1191	735.74	512	0.5788	790.51	1085	0.8882	851.72	492
0.2077	744.03	755	0.6343	799.52	1052	0.9267	861.64	345
0.2921	752.82	921	0.6912	809.56	982	0.9583	870.20	222
0.3727	762.12	1023	0.7504	820.85	888	1.0000	882.54	0
T = 318.15 K								
Propyl Ethanoate (1) + Hexane (2)								
0.0000	636.65	0	0.3318	700.54	710	0.6815	778.85	541
0.0304	641.69	197	0.3997	714.87	734	0.7426	793.66	456
0.0796	650.67	354	0.4505	725.91	723	0.7992	807.68	368
0.1381	661.70	494	0.5124	739.66	693	0.8648	824.39	242
0.2079	675.31	608	0.5708	752.92	652	0.9227	839.28	151
0.2642	686.58	674	0.6220	764.76	609	1.0000	859.78	0
Propyl Ethanoate (1) + Heptane (2)								
0.0000	662.06	0	0.3638	718.84	867	0.7260	791.42	671
0.0291	666.08	118	0.4295	730.78	886	0.7727	802.14	588
0.0843	673.91	325	0.4902	742.29	877	0.7949	807.68	496
0.1595	685.14	544	0.5530	754.61	858	0.8645	824.39	369
0.2300	696.25	694	0.6057	765.37	820	0.9242	839.28	260
0.2972	707.31	805	0.6734	779.75	749	1.0000	859.78	0
Propyl Ethanoate (1) + Octane (2)								
0.0000	682.17	0	0.3866	732.28	967	0.7422	796.76	765
0.0440	687.06	175	0.4471	741.75	1014	0.7792	804.84	683
0.0919	692.49	371	0.5188	753.71	1025	0.8435	819.52	530
0.1675	701.73	596	0.5695	762.78	985	0.8743	826.88	449
0.2438	711.68	776	0.6293	773.93	932	0.9284	840.49	273
0.3148	721.61	889	0.6793	783.75	868	1.0000	859.78	0
Propyl Ethanoate (1) + Nonane (2)								
0.0000	698.06	0	0.4077	742.85	1062	0.7597	801.71	828
0.0217	699.96	101	0.4731	752.08	1094	0.8179	814.08	686

Table 5. continued

$x_1$	$\rho$ kg·m <sup>-3</sup>	$10^9 \cdot v^E$ m <sup>3</sup> ·mol <sup>-1</sup>	$x_1$	$\rho$ kg·m <sup>-3</sup>	$10^9 \cdot v^E$ m <sup>3</sup> ·mol <sup>-1</sup>	$x_1$	$\rho$ kg·m <sup>-3</sup>	$10^9 \cdot v^E$ m <sup>3</sup> ·mol <sup>-1</sup>
Propyl Ethanoate (1) + Nonane (2)								
0.1046	707.72	424	0.5367	761.66	1105	0.8565	822.81	574
0.1791	715.36	648	0.5943	771.02	1073	0.8964	832.40	430
0.2659	724.95	872	0.6526	781.18	1008	0.9373	842.73	275
0.3350	733.37	976	0.7078	791.39	934	1.0000	859.78	0
Propyl Ethanoate (1) + Decane (2)								
0.0000	710.90	0	0.4333	752.19	1136	0.7733	805.48	865
0.0640	715.53	320	0.4936	759.95	1161	0.8247	816.07	726
0.1164	719.72	524	0.5563	768.63	1167	0.8670	825.48	584
0.1961	726.75	755	0.6213	778.51	1122	0.9092	835.51	427
0.2794	734.84	944	0.6781	787.96	1041	0.9463	844.94	269
0.3548	742.92	1064	0.7226	795.79	980	1.0000	859.78	0
T = 328.15 K								
Propyl Ethanoate (1) + Hexane (2)								
0.0000	627.21	0	0.3322	690.12	803	0.6944	770.81	582
0.0253	631.33	173	0.3986	704.04	816	0.7605	786.79	484
0.0749	640.18	356	0.4614	717.55	805	0.8114	799.39	396
0.1369	651.64	528	0.5209	730.74	763	0.8707	814.35	288
0.2052	664.70	665	0.5809	744.27	719	0.9235	828.02	174
0.2719	677.82	764	0.6200	753.31	673	1.0000	848.30	0
Propyl Ethanoate (1) + Heptane (2)								
0.0000	653.72	0	0.3783	711.79	960	0.7560	787.53	669
0.0373	658.49	226	0.4478	724.30	982	0.8074	799.52	547
0.0866	665.39	411	0.5142	736.83	966	0.8560	811.20	428
0.1645	676.84	643	0.5756	748.92	927	0.9097	824.69	266
0.2401	688.62	800	0.6377	761.72	853	0.9638	838.67	109
0.3096	699.98	904	0.6884	772.52	785	1.0000	848.30	0
Propyl Ethanoate (1) + Octane (2)								
0.0000	674.14	0	0.4000	724.96	1066	0.7686	791.91	758
0.0249	676.67	143	0.4761	736.96	1093	0.8149	802.10	647
0.1032	685.41	454	0.5341	746.69	1080	0.8651	813.78	496
0.1801	694.64	697	0.5975	757.93	1037	0.9233	828.00	310
0.2554	704.35	873	0.6603	769.72	968	0.9404	832.41	241
0.3244	713.85	988	0.7147	780.66	859	1.0000	848.30	0
Propyl Ethanoate (1) + Nonane (2)								
0.0000	690.17	0	0.4290	736.68	1127	0.7857	796.76	791
0.0560	695.08	247	0.4999	746.72	1149	0.8318	806.59	667
0.1062	699.77	435	0.5709	757.63	1126	0.8801	817.62	503
0.1918	708.26	730	0.6217	765.98	1086	0.8853	818.82	488
0.2757	717.52	919	0.6881	777.69	999	0.9429	832.95	273
0.3519	726.64	1049	0.7461	788.66	901	1.0000	848.30	0
Propyl Ethanoate (1) + Decane (2)								
0.0000	703.34	0	0.4553	745.99	1218	0.8204	804.55	801
0.0485	706.59	286	0.5227	754.73	1227	0.8511	811.22	678
0.1075	711.11	524	0.5818	763.01	1214	0.8851	818.81	560
0.1960	718.63	797	0.6506	773.58	1148	0.9321	830.23	343
0.2952	728.02	1038	0.7058	782.86	1058	0.9580	836.88	218
0.3758	736.64	1150	0.7598	792.64	949	1.0000	848.30	0

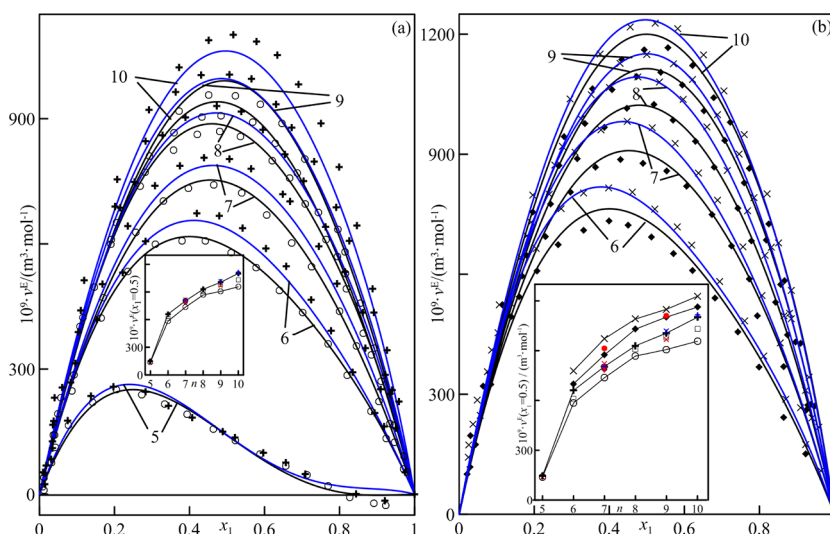
<sup>a</sup>Uncertainties  $u$  are:  $u(T) = \pm 0.02$  K,  $u(\rho) = \pm 0.02$  kg·m<sup>-3</sup>,  $u(x) = \pm 0.0005$ ,  $u(10^9 v^E) = \pm 2$  m<sup>3</sup>·mol<sup>-1</sup>.

the values of  $h^E$  presented uncertainties of less than 1 %, and considering an uncertainty of  $\pm 0.0005$  for the molar fraction. No certified  $h^E$  values for calibrating at the temperature of 291.15 K was found.

Refractive indices for the pure products were measured with a 320 Zuzi refractometer, with a reading error of  $\pm 0.0002$  units in  $n_D$ . The temperature was maintained constant around ( $T \pm 0.01$ ) K with the circulating water bath mentioned above.

## PRESENTATION AND TREATMENT OF RESULTS

**Vapor Pressures.** In previous works of this series on mixtures of alkyl ethanoates with alkanes, it was proposed to measure the vapor pressures of the pure substances to verify the quality of the data available in the literature, because of the influence of these values, or their correlations, on VLE calculations. So, values of  $(T, p_i^o)$  and their correlations were published previously<sup>3</sup> for hydrocarbons (C<sub>6</sub>–C<sub>10</sub>), extending in some cases the range of quantities measured. Propyl ethanoate is the compound



**Figure 2.** Excess molar volumes and correlation curves (—) obtained by eq 3 at the temperatures of: (a) 291.15 K, ○, black line; 298.15 K, +, blue line. (b) 318.15 K, ◆, black line; 328.15 K, ×, blue line. Inset figures show the equimolar  $v^E$  values vs  $n$  ( $C_nH_{2n+2}$ ) obtained in this work and their comparison with those from literature referenced: at  $T = 298.15$  K: red ×, ref 4; blue ×, ref 6; □, ref 7; red +, ref 9; blue +, ref 10; red ◆, ref 11; at  $T = 318.15$  K: red ●, ref 5.

common to the mixtures in this work, and the curve  $p_i^o = \phi(T)$  was obtained previously;<sup>27</sup> however, in the experimentation, some discrepancies were observed when the acentric factor calculated from vapor pressure data was compared to values recorded in the literature. Figure 1a shows the differences between the data measured here and those published,<sup>27</sup> especially in the interval  $T < 360$  K. The differences in relation to those published by Farková and Witcherle<sup>30</sup> were smaller. These facts, together with the above discrepancy for the acentric factor, justify making new measurements to establish a more precise saturation curve. Experimental values ( $T, p_i^o$ ) are presented in Table 3, and they were correlated with Antoine's equation. Optimum values for  $A$ ,  $B$  and  $C$  coefficients were obtained after applying a linear-regression procedure (varying the  $C$ -value to get the optimum fit) minimizing the standard deviation  $s(p_i^o)$  of the pressure data; the results are recorded in Table 4.

By using the theorem of the corresponding states, a modified version of Antoine's equation is obtained when reduced quantities are used, which has a similar format to the original equation

$$\log p_{i,r}^o = a - b/(T_r - c) \quad (2)$$

Coefficients  $a$ ,  $b$ , and  $c$  were determined by a same procedure indicated above but with experimental data in reduced coordinates; the coefficients obtained appear in brackets in Table 4. A previous work<sup>28</sup> described in detail the relationships existing between both types of coefficients, which would be identical if Antoine's equation were valid over the entire range of the saturation curve (up to the critical point), since the boundary conditions for the critical point are implicit to eq 2. The values for  $a$ ,  $b$ , and  $c$  permit calculate the acentric factor of the ester, introducing eq 2 in the Pitzer expression,<sup>29</sup> which produces:  $(0.7 - c)(\omega + a + 1) = b$ . This value is shown in Table 2 and is similar to published values<sup>27</sup> and that determined by the Lee–Kesler method.<sup>31</sup> The differences in relation to those published by Farková and Witcherle<sup>30</sup> were smaller; see Figure 1a. Figure 1b shows the straight-lines of vapor pressures in reduced coordinates for propyl ethanoate and heptane and the azeotropic points for the corresponding mixture, which we

discuss later. The inset compares the vapor pressure lines in reduced coordinates for the first three ethanoates and alkanes, revealing their tendency to converge toward the so-called “infinite point”.

**Excess Properties.** For all of the binary systems, established empirically as:  $H_3CCOOC_3H_7$  (1) +  $C_nH_{2n+2}$  (2) ( $n = 5$  to 10), the excess volumes  $v^E$  were determined from the mixing densities, which are prepared by weighing. Measurements were recorded at four temperatures, (291.15, 298.15, 318.15, and 328.15) K, except for mixtures containing pentane, since its boiling point limits working with this product to just the first two temperatures. Experimental points ( $x_1, \rho, v^E$ ) are found in Table 5 and the corresponding representations in Figure 2a,b. The inset figures show the comparison between the equimolar values obtained here and those from literature, including those published previously by our research team.<sup>4–6</sup> In general, there is good agreement with the exception of the value corresponding to the propyl ethanoate + decane system at 298.15 K,<sup>7</sup> which has a much lower value than the one obtained here. However, new values of  $v^E$  were determined for all of the mixtures in an attempt to achieve correlations for the densities, eq 1, which are used to determine the VLE compositions. The  $h^E$  values were measured for the six systems at  $T = (291.15, 298.15, \text{ and } 318.15)$  K, but only for mixtures with even alkanes since values for mixtures with  $n = 5, 7$ , and  $9$  were already published.<sup>4,5</sup> The  $(x_1, h^E)$  values are recorded in Table 6 and represented graphically in Figure 3a,b; the inset figures show the comparison between the equimolar values with the values taken from the literature. On the whole, there is good agreement except for the measurements of some authors,<sup>11–13</sup> which present slightly lower values.

Correlations were carried out for  $v^E$  and  $h^E$ , Tables 5 and 6, versus the *active fraction* of the property considered, related to the ester  $z_1(x_1, T)$  by a simple polynomial expression whose previous have been acceptable, which for a generic excess function  $y^E$  takes the following form:

$$y^E = z_1(1 - z_1) \sum_{i=0}^{i=2} \left( \frac{y_{i0}}{T} + y_{i1} + y_{i2}T \right) z_1^i \quad (3)$$

Table 6. Experimental Values of  $(x_1, h^E)$  for Binary Systems  $\text{CH}_3\text{COO}(\text{CH}_2)_2\text{CH}_3$  (1) +  $\text{C}_n\text{H}_{2n+2}$  ( $n = 5$  to 10) (2) at Three Temperatures of (291.15, 298.15, and 318.15) K and Atmospheric Pressure<sup>a</sup>

$x_1$	$h^E$ J·mol <sup>-1</sup>	$x_1$	$h^E$ J·mol <sup>-1</sup>	$x_1$	$h^E$ J·mol <sup>-1</sup>	$x_1$	$h^E$ J·mol <sup>-1</sup>	$x_1$	$h^E$ J·mol <sup>-1</sup>	$x_1$	$h^E$ J·mol <sup>-1</sup>
T = 291.15 K						Propyl Ethanoate (1) + Hexane (2)					
Propyl Ethanoate (1) + Pentane (2)						0.1450	529	0.5590	1094	0.8989	376
0.0667	224	0.4028	988	0.6434	896	0.2223	743	0.6073	1044	0.9494	195
0.1334	406	0.4610	1026	0.7089	787	0.3011	931	0.6518	979		
0.2047	617	0.5088	1031	0.7812	636	0.3660	1038	0.7091	874		
0.2753	780	0.5257	1025	0.8537	446	Propyl Ethanoate (1) + Octane (2)					
0.3414	914	0.5824	973	0.9242	249	0.0883	429	0.4117	1219	0.6055	1199
Propyl Ethanoate (1) + Hexane (2)						0.1747	727	0.4788	1257	0.6550	1139
0.0740	275	0.4417	1087	0.6705	952	0.2568	966	0.5346	1249	0.7074	1049
0.1514	544	0.4984	1109	0.7361	817	0.3398	1130	0.5849	1219	0.7607	929
0.2307	751	0.5492	1090	0.8064	655	Propyl Ethanoate (1) + Decane (2)					
0.3056	922	0.5528	1087	0.8762	464	0.1028	532	0.5348	1416	0.7601	1076
0.3758	1038	0.6101	1029	0.9422	246	0.2102	889	0.5925	1395	0.8123	898
Propyl Ethanoate (1) + Heptane (2)						0.3062	1158	0.6163	1363	0.8626	707
0.0996	436	0.5309	1195	0.7717	810	0.3924	1317	0.6615	1305	0.9119	492
0.2001	756	0.5880	1149	0.8326	639	0.4676	1394	0.7100	1195	0.9581	259
0.2956	1001	0.6380	1073	0.8942	437	T = 318.15 K					
0.3852	1140	0.6560	1046	0.9501	226	Propyl Ethanoate (1) + Hexane (2)					
0.4642	1192	0.7113	948			0.0748	289	0.4746	1146	0.7753	774
Propyl Ethanoate (1) + Octane (2)						0.1298	511	0.5084	1142	0.8288	613
0.0879	457	0.4860	1298	0.7256	1020	0.2004	736	0.5582	1127	0.8906	417
0.1784	765	0.5436	1292	0.7843	862	0.2777	941	0.6039	1080	0.9452	224
0.2664	1014	0.5927	1257	0.8412	686	0.3479	1058	0.6543	1012		
0.3472	1175	0.6180	1219	0.8983	469	0.4119	1119	0.7123	914		
0.4208	1265	0.6703	1139	0.9546	233	Propyl Ethanoate (1) + Octane (2)					
Propyl Ethanoate (1) + Nonane (2)						0.0767	394	0.5293	1296	0.7936	864
0.1167	596	0.5009	1383	0.7299	1085	0.1676	740	0.5791	1257	0.8521	682
0.2247	946	0.5447	1371	0.7964	899	0.2591	1018	0.5859	1248	0.9064	476
0.3093	1167	0.5617	1359	0.8649	648	0.3352	1179	0.6316	1191	0.9555	249
0.3790	1298	0.6139	1312	0.9356	355	0.4086	1276	0.6848	1108		
0.4448	1360	0.6683	1222			0.4719	1304	0.7377	1001		
Propyl Ethanoate (1) + Decane (2)						Propyl Ethanoate (1) + Decane (2)					
0.0703	391	0.4892	1457	0.7166	1228	0.1083	556	0.5203	1454	0.7682	1083
0.1623	752	0.5501	1460	0.7751	1056	0.2064	922	0.5710	1432	0.8288	885
0.2528	1061	0.6049	1428	0.8324	844	0.3068	1211	0.6098	1391	0.8862	640
0.3401	1276	0.6150	1413	0.8924	585	0.3885	1364	0.6588	1329	0.9480	347
0.4179	1399	0.6649	1337	0.9524	309	0.4625	1446	0.7129	1225		
T = 298.15 K						Propyl Ethanoate (1) + Hexane (2)					
0.0319	103	0.4223	1104	0.7653	741						
0.0736	271	0.5030	1122	0.8334	569						

<sup>a</sup>Uncertainties  $u$  are:  $u(T) = \pm 0.002$  K,  $u(x) = \pm 0.0005$ , and  $u(h^E) = \pm 2$  J·mol<sup>-1</sup>.

For the volumes, their dependence on the composition of the mixtures is determined by the *volume active fraction*  $z_1$ , given by the expression,

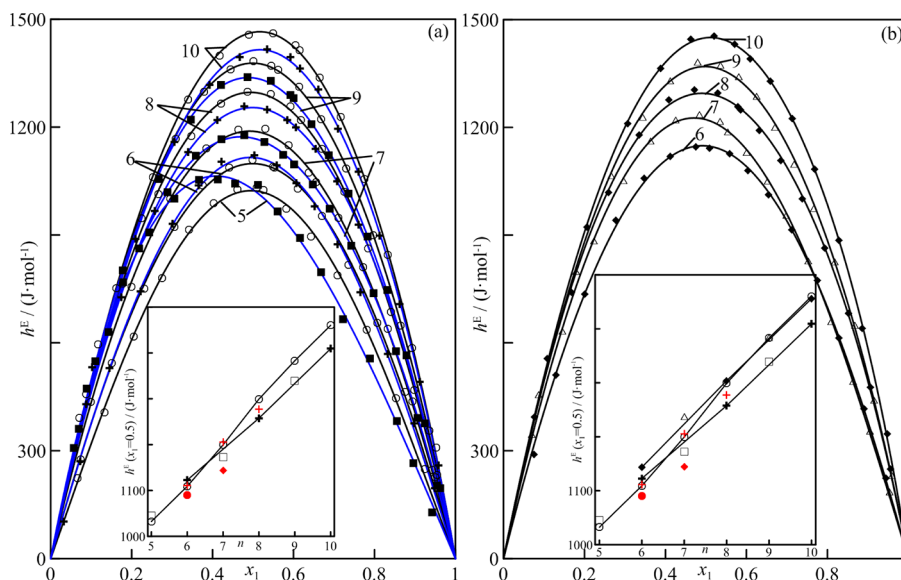
$$\begin{aligned}
 z_1 &= \frac{x_1}{x_1 + [v_2^0(T)/v_1^0(T)]x_2} \\
 &= \frac{x_1}{x_1 + k_v^{21}(T)x_2} \\
 &= \frac{x_1}{x_1 + [M_2\rho_1/M_1\rho_2](T)x_2} \quad (4)
 \end{aligned}$$

where  $M_i$  and  $\rho_i$  are, respectively, the molecular masses and densities of the pure component  $i$ . The so-called active fraction  $z_1$  coincides, eq 4, with the expression of the volumetric

fraction, although this latter concept is not used in the correlation of other properties. The values of  $k_v^{21}(T)$  vary with the working temperature, although, in some mixtures this is negligible; so, in this case the slope varies from a slightly positive value in mixtures with pentane ( $dk_v^{21}/dT = 4.4 \cdot 10^{-4} \text{ K}^{-1}$ ) to a negative value of  $-3.9 \cdot 10^{-4} \text{ K}^{-1}$  in mixtures with decane. Therefore, to simplify the data treatment, a constant mean value is taken for  $k_v^{21}$ , which is calculated as shown in eq 4, since the greatest difference (in the variation in  $T$ ) is less than 0.4 %.

When eq 3 is used to correlate the enthalpy data  $h^E(x_1, T)$ , there is considered to be a dependence on the energetic effects arising during the mixing process, taking into account the contact intermolecular surfaces. Hence, eq 4 should be considered as a function of “*surface active fractions*” assigning a





**Figure 3.** Excess molar enthalpies and correlation curves (—) obtained by eq 3 at the temperatures of: (a) 291.15 K, O, black line; 298.15 K, +, blue line. (b) 318.15 K, ◆, black line. Inset figures show the equimolar  $h^E$  values vs  $n$  ( $C_nH_{2n+2}$ ) obtained in this work and their comparison with those from literature referenced: at  $T = 298.15$  K: □, ref 4; red ●, ref 11; red +, ref 12; red ◆, ref 13; at  $T = 318.15$  K: △, ref 5.

**Table 7.** Coefficients  $y_{ij}$  and  $k$  and Standard Deviations  $s(y^E)$  Obtained in the Correlation of Experimental  $10^9 v^E(x_1, T)$  and  $h^E(x_1, T)$  Data at Various Temperatures, for Binaries  $CH_3COO(CH_2)_2CH_3$  (1) +  $C_nH_{2n+2}$  ( $n = 5$  to 10) (2) Using eqs 3 to 5

propyl ethanoate +	pentane	hexane	heptane	octane	nonane	decane
$y_{ij} \rightarrow v_{ij}$						
$v_{00}$	$3.689 \cdot 10^6$	$3.688 \cdot 10^7$	$2.561 \cdot 10^7$	$2.730 \cdot 10^7$	$-9.556 \cdot 10^6$	$-2.871 \cdot 10^7$
$v_{01}$	$-3.287 \cdot 10^4$	$-2.488 \cdot 10^5$	$-1.759 \cdot 10^5$	$-1.788 \cdot 10^5$	$6.086 \cdot 10^4$	$1.787 \cdot 10^5$
$v_{02}$	$7.770 \cdot 10^1$	$4.336 \cdot 10^2$	$3.173 \cdot 10^2$	$3.119 \cdot 10^2$	$-7.526 \cdot 10^1$	$-2.527 \cdot 10^2$
$v_{10}$	$2.234 \cdot 10^6$	$-1.449 \cdot 10^8$	$-6.054 \cdot 10^7$	$-6.531 \cdot 10^7$	$2.036 \cdot 10^7$	$7.679 \cdot 10^7$
$v_{11}$	$2.037 \cdot 10^4$	$9.601 \cdot 10^5$	$4.113 \cdot 10^5$	$4.184 \cdot 10^5$	$-1.371 \cdot 10^5$	$-4.826 \cdot 10^5$
$v_{12}$	$-1.135 \cdot 10^2$	$-1.605 \cdot 10^3$	$-7.123 \cdot 10^2$	$-6.890 \cdot 10^2$	$2.076 \cdot 10^2$	$7.264 \cdot 10^2$
$v_{20}$	$-2.612 \cdot 10^5$	$1.193 \cdot 10^8$	$1.904 \cdot 10^7$	$3.369 \cdot 10^7$	$-5.274 \cdot 10^7$	$-1.050 \cdot 10^8$
$v_{21}$	$-3.634 \cdot 10^4$	$-7.880 \cdot 10^5$	$-1.358 \cdot 10^5$	$-2.137 \cdot 10^5$	$3.418 \cdot 10^5$	$6.643 \cdot 10^5$
$v_{22}$	$1.365 \cdot 10^2$	$1.307 \cdot 10^3$	$2.476 \cdot 10^2$	$3.483 \cdot 10^2$	$-5.420 \cdot 10^2$	$-1.032 \cdot 10^3$
$k_v^{21}$	1.071	1.138	1.274	1.411	1.549	1.688
$s(291.15 \text{ K})$	15	8	15	16	24	19
$s(298.15 \text{ K})$	19	16	25	17	29	59
$s(318.15 \text{ K})$		34	20	10	11	30
$s(328.15 \text{ K})$		18	20	10	7	27
$y_{ij} \rightarrow h_{ij}$						
$h_{00}$	$1.151 \cdot 10^7$	$3.733 \cdot 10^7$	$-1.322 \cdot 10^8$	$4.898 \cdot 10^7$	$-1.323 \cdot 10^7$	$6.605 \cdot 10^7$
$h_{01}$	$-1.850 \cdot 10^5$	$-2.462 \cdot 10^5$	$8.707 \cdot 10^5$	$-3.194 \cdot 10^5$	$9.473 \cdot 10^4$	$-4.296 \cdot 10^5$
$h_{02}$	$5.106 \cdot 10^2$	$4.198 \cdot 10^2$	$-1.411 \cdot 10^3$	$5.429 \cdot 10^2$	$-1.423 \cdot 10^2$	$7.250 \cdot 10^2$
$h_{10}$	$-5.440 \cdot 10^7$	$-1.942 \cdot 10^8$	$5.891 \cdot 10^8$	$-6.075 \cdot 10^6$	$1.474 \cdot 10^8$	$-9.318 \cdot 10^7$
$h_{11}$	$6.875 \cdot 10^5$	$1.286 \cdot 10^6$	$-3.874 \cdot 10^6$	$5.348 \cdot 10^4$	$-9.732 \cdot 10^5$	$6.244 \cdot 10^5$
$h_{12}$	$-1.707 \cdot 10^3$	$-2.122 \cdot 10^3$	$6.349 \cdot 10^3$	$-1.269 \cdot 10^2$	$1.583 \cdot 10^3$	$-1.068 \cdot 10^3$
$h_{20}$	$6.265 \cdot 10^5$	$2.281 \cdot 10^8$	$-5.508 \cdot 10^8$	$-6.858 \cdot 10^7$	$-9.367 \cdot 10^7$	$5.732 \cdot 10^7$
$h_{21}$	$-1.986 \cdot 10^5$	$-1.506 \cdot 10^6$	$3.631 \cdot 10^6$	$4.337 \cdot 10^5$	$6.163 \cdot 10^5$	$-3.940 \cdot 10^5$
$h_{22}$	$6.612 \cdot 10^2$	$2.475 \cdot 10^3$	$-5.973 \cdot 10^3$	$-6.757 \cdot 10^2$	$-1.003 \cdot 10^3$	$6.853 \cdot 10^2$
$k_v^{21}$	1.002	1.049	1.176	1.303	1.431	1.559
$s(291.15 \text{ K})$	11	12	8	11	11	16
$s(298.15 \text{ K})$	13	12	9	6	9	17
$s(318.15 \text{ K})$		9	7	9	11	12

surface parameter  $\zeta_i$  (proportional to the surface of each molecule), which describes its specific contribution to the "excess quantity" produced.

$$z_1 = \frac{x_1}{x_1 + [\zeta_2^0(T)/\zeta_1^0(T)]x_2} = \frac{x_1}{x_1 + k_h^{21}(T)x_2} \quad (5)$$

The relationship between the  $k$  parameters of eqs 4 and 5 is established by an equation of the form:

$$k_h^{21} = (k_q^{21}) \left( \frac{k_v^{21}}{k_r^{21}} \right)^{2/3} \quad (6)$$

Table 8. Experimental ( $T, x_1, y_1$ ) Data and Calculated Quantities for Characterizing the iso- $p$  VLE of Binaries Propyl Ethanoate (1) + an Alkane (2) at 101.32 kPa<sup>a</sup>

$T/K$	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$	$g^E/RT$	$T/K$	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$	$g^E/RT$
Propyl Ethanoate (1) + Pentane (2)											
309.24	0.0000	0.0000		1.000	0.000	341.02	0.7819	0.2622	1.020	1.361	0.083
309.88	0.0146	0.0061	4.773	0.988	0.011	344.98	0.8189	0.3160	1.013	1.377	0.069
310.21	0.0276	0.0102	4.140	0.986	0.026	348.96	0.8530	0.3782	1.008	1.402	0.056
310.83	0.0579	0.0170	3.255	0.991	0.060	352.67	0.8810	0.4411	0.999	1.427	0.041
311.59	0.1101	0.0241	2.330	1.016	0.107	357.79	0.9150	0.5433	0.995	1.455	0.027
312.60	0.1455	0.0303	2.100	1.019	0.124	362.12	0.9401	0.6420	0.994	1.473	0.018
313.21	0.1744	0.0352	1.985	1.029	0.143	366.04	0.9615	0.7451	0.996	1.503	0.012
313.91	0.2135	0.0400	1.793	1.051	0.164	368.43	0.9734	0.8131	0.997	1.520	0.008
316.48	0.3165	0.0574	1.529	1.098	0.198	370.32	0.9817	0.8650	0.993	1.535	0.001
319.77	0.4148	0.0791	1.392	1.134	0.211	372.10	0.9902	0.9250	0.998	1.537	0.002
324.20	0.5263	0.1092	1.245	1.190	0.198	373.21	0.9951	0.9611	0.998	1.565	0.000
330.46	0.6412	0.1542	1.109	1.251	0.147	374.34	1.0000	1.0000	1.000		0.000
336.62	0.7303	0.2110	1.042	1.317	0.104						
Propyl Ethanoate (1) + Hexane (2)											
341.89	0.0000	0.0000		1.000	0.000	352.13	0.6403	0.3396	1.078	1.368	0.161
341.95	0.0088	0.0070	2.341	1.000	0.007	352.98	0.6643	0.3599	1.069	1.388	0.154
342.07	0.0253	0.0196	2.269	1.000	0.021	353.97	0.6922	0.3833	1.056	1.420	0.146
342.25	0.0470	0.0354	2.191	1.001	0.038	355.22	0.7209	0.4104	1.040	1.447	0.131
342.50	0.0767	0.0540	2.028	1.006	0.060	356.36	0.7493	0.4371	1.026	1.492	0.120
342.91	0.1100	0.0715	1.843	1.012	0.078	357.75	0.7772	0.4721	1.020	1.517	0.108
343.32	0.1485	0.0905	1.702	1.023	0.098	359.48	0.8080	0.5161	1.013	1.542	0.094
343.84	0.1959	0.1100	1.538	1.044	0.119	361.45	0.8422	0.5680	1.003	1.592	0.076
344.43	0.2372	0.1301	1.469	1.058	0.134	363.46	0.8746	0.6264	0.998	1.646	0.061
345.08	0.2860	0.1492	1.364	1.084	0.146	365.36	0.9015	0.6857	0.999	1.681	0.050
345.80	0.3385	0.1699	1.279	1.118	0.157	367.41	0.9265	0.7465	0.992	1.727	0.033
346.64	0.3866	0.1959	1.252	1.140	0.167	368.79	0.9423	0.7914	0.991	1.750	0.024
347.46	0.4332	0.2175	1.204	1.173	0.171	370.65	0.9629	0.8567	0.993	1.788	0.015
348.30	0.4773	0.2415	1.177	1.204	0.175	372.07	0.9787	0.9082	0.992	1.929	0.006
349.16	0.5184	0.2641	1.149	1.237	0.174	373.16	0.9899	0.9507	0.994	2.129	0.002
350.20	0.5629	0.2904	1.122	1.277	0.172	374.34	1.0000	1.0000	1.000		0.000
351.25	0.6104	0.3179	1.091	1.337	0.166						
Propyl Ethanoate (1) + Heptane (2)											
371.55	0.0000	0.0000		1.000	0.000	367.64	0.6001	0.5341	1.089	1.303	0.157
370.51	0.0298	0.0603	2.275	0.997	0.022	367.79	0.6279	0.5521	1.071	1.340	0.152
370.13	0.0590	0.1033	1.990	0.992	0.033	367.90	0.6498	0.5686	1.062	1.367	0.149
369.57	0.0954	0.1513	1.833	0.992	0.051	368.19	0.6729	0.5869	1.049	1.390	0.140
368.86	0.1398	0.2084	1.760	0.993	0.073	368.44	0.7003	0.6065	1.034	1.435	0.132
368.29	0.1895	0.2627	1.665	0.998	0.095	368.74	0.7306	0.6301	1.020	1.489	0.122
367.78	0.2337	0.3031	1.582	1.012	0.116	369.06	0.7556	0.6507	1.008	1.536	0.111
367.46	0.2761	0.3347	1.493	1.032	0.133	369.43	0.7801	0.6762	1.004	1.566	0.102
367.27	0.3070	0.3578	1.444	1.047	0.145	369.85	0.8033	0.7023	0.999	1.591	0.091
367.11	0.3411	0.3828	1.397	1.063	0.154	370.29	0.8275	0.7289	0.994	1.632	0.080
367.08	0.3789	0.4073	1.341	1.086	0.162	370.75	0.8508	0.7561	0.989	1.676	0.068
367.07	0.4138	0.4308	1.299	1.105	0.167	371.26	0.8823	0.7959	0.988	1.753	0.055
367.05	0.4450	0.4470	1.257	1.129	0.169	371.73	0.9069	0.8321	0.991	1.800	0.047
367.12	0.4716	0.4624	1.219	1.154	0.169	372.54	0.9372	0.8805	0.990	1.857	0.029
367.23	0.5025	0.4781	1.179	1.187	0.168	373.25	0.9652	0.9292	0.994	1.948	0.017
367.35	0.5492	0.5014	1.127	1.247	0.165	373.98	0.9912	0.9712	0.990	3.072	0.000
367.46	0.5694	0.5155	1.114	1.265	0.163	374.34	1.0000	1.0000	1.000		
Propyl Ethanoate (1) + Octane (2)											
398.85	0.0000	0.0000		1.000	0.000	375.17	0.7735	0.8285	1.045	1.490	0.124
394.46	0.0553	0.1455	1.523	1.016	0.038	375.07	0.7899	0.8386	1.039	1.516	0.118
391.36	0.1003	0.2423	1.513	1.030	0.068	374.89	0.8078	0.8500	1.035	1.549	0.112
389.47	0.1319	0.2986	1.489	1.041	0.087	374.83	0.8165	0.8547	1.032	1.575	0.109
386.59	0.1931	0.3968	1.459	1.046	0.109	374.77	0.8309	0.8643	1.027	1.599	0.102
384.48	0.2438	0.4619	1.424	1.058	0.129	374.64	0.8455	0.8736	1.024	1.637	0.096
382.65	0.3092	0.5235	1.338	1.082	0.144	374.54	0.8577	0.8816	1.022	1.670	0.092
381.89	0.3414	0.5482	1.295	1.100	0.151	374.46	0.8709	0.8906	1.019	1.705	0.085
380.14	0.4125	0.6088	1.250	1.125	0.161	374.42	0.8829	0.8993	1.016	1.733	0.078

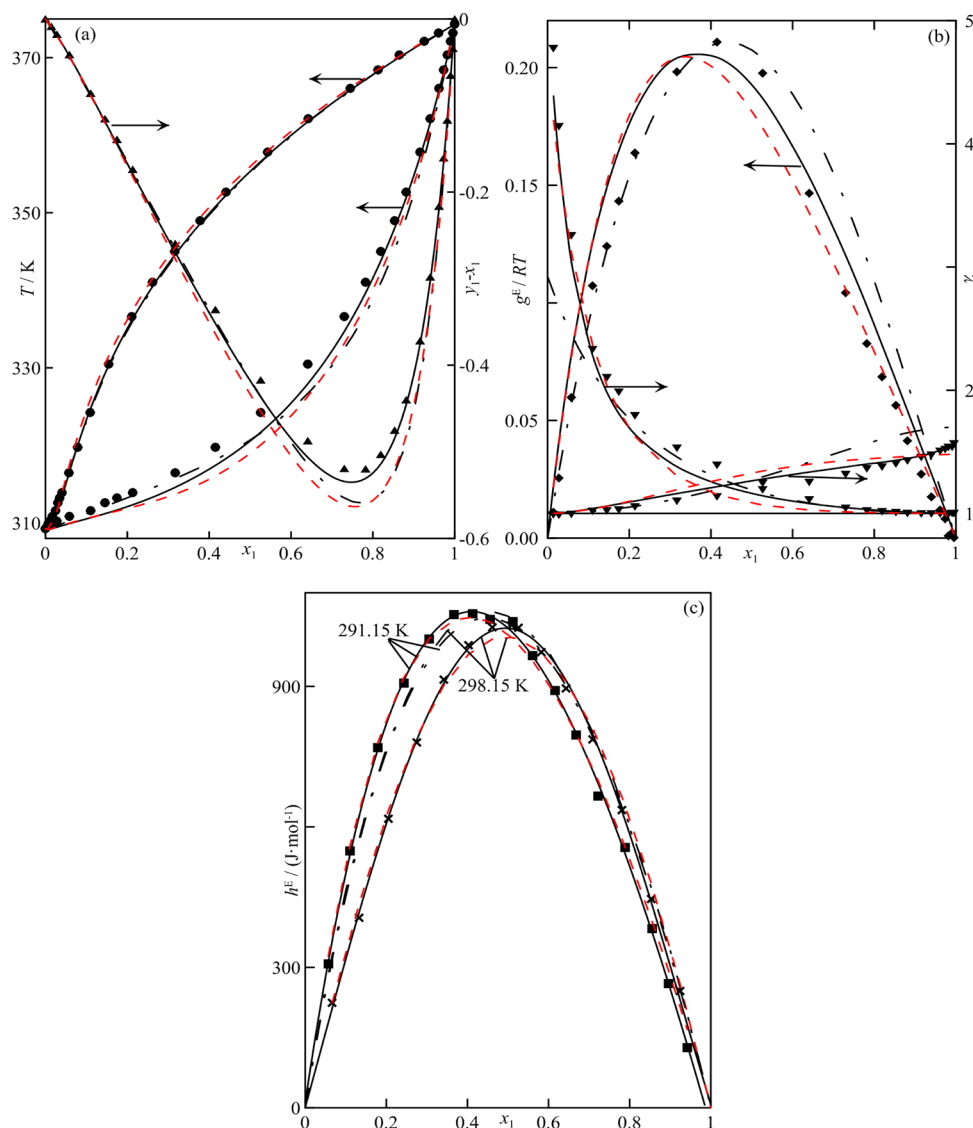
Table 8. continued

T/K	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$	$g^E/RT$	T/K	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$	$g^E/RT$
Propyl Ethanoate (1) + Octane (2)											
378.44	0.4913	0.6653	1.203	1.170	0.171	374.39	0.8949	0.9081	1.013	1.764	0.071
377.58	0.5447	0.6986	1.168	1.209	0.171	374.37	0.9050	0.9158	1.011	1.789	0.065
377.31	0.5692	0.7115	1.147	1.233	0.168	374.36	0.9146	0.9234	1.009	1.811	0.059
376.99	0.5886	0.7228	1.137	1.253	0.168	374.35	0.9246	0.9315	1.007	1.835	0.052
376.84	0.6019	0.7308	1.129	1.263	0.166	374.34	0.9344	0.9393	1.005	1.870	0.046
376.67	0.6168	0.7410	1.123	1.269	0.163	374.32	0.9532	0.9557	1.003	1.915	0.033
376.11	0.6732	0.7712	1.088	1.338	0.152	374.31	0.9628	0.9636	1.001	1.980	0.026
376.03	0.6918	0.7792	1.072	1.372	0.146	374.31	0.9730	0.9731	1.001	2.016	0.020
375.79	0.7113	0.7909	1.066	1.398	0.142	374.32	0.9833	0.9829	1.000	2.072	0.012
375.58	0.7295	0.8025	1.061	1.418	0.138	374.33	0.9914	0.9909	0.999	2.140	0.006
375.37	0.7528	0.8157	1.051	1.458	0.131	374.34	1.0000	1.0000	1.000		0.000
Propyl Ethanoate (1) + Nonane (2)											
423.94	0.0000	0.0000		1.000	0.000	383.46	0.5720	0.8381	1.131	1.203	0.149
422.45	0.0127	0.0577	1.382	0.998	0.003	382.34	0.6152	0.8531	1.104	1.258	0.149
420.60	0.0250	0.1133	1.432	0.996	0.006	381.35	0.6546	0.8673	1.084	1.309	0.146
418.03	0.0444	0.1855	1.394	0.997	0.012	380.41	0.6949	0.8818	1.066	1.361	0.138
414.85	0.0722	0.2671	1.318	1.003	0.023	379.60	0.7311	0.8943	1.051	1.419	0.131
411.13	0.1076	0.3537	1.277	1.015	0.040	378.81	0.7702	0.9067	1.035	1.504	0.120
407.09	0.1490	0.4470	1.278	1.017	0.051	377.99	0.8112	0.9224	1.023	1.566	0.103
403.33	0.1913	0.5268	1.280	1.017	0.061	377.21	0.8507	0.9359	1.012	1.679	0.088
399.70	0.2419	0.5915	1.241	1.039	0.082	376.55	0.8853	0.9505	1.007	1.726	0.068
396.20	0.2952	0.6524	1.222	1.055	0.097	376.01	0.9151	0.9624	1.001	1.805	0.051
394.25	0.3240	0.6851	1.228	1.056	0.103	375.59	0.9373	0.9701	0.998	2.020	0.042
392.13	0.3624	0.7188	1.216	1.066	0.112	375.23	0.9577	0.9767	0.993	2.362	0.030
390.12	0.4017	0.7490	1.205	1.079	0.120	374.88	0.9749	0.9843	0.994	2.715	0.019
389.02	0.4245	0.7647	1.198	1.088	0.125	374.65	0.9873	0.9899	0.993	3.469	0.009
387.13	0.4703	0.7903	1.175	1.118	0.135	374.50	0.9949	0.9955	0.996	3.945	0.003
385.53	0.5126	0.8107	1.154	1.155	0.144	374.34	1.0000	1.0000	1.000		0.000
384.63	0.5346	0.8226	1.151	1.166	0.147						
Propyl Ethanoate (1) + Decane (2)											
447.27	0.0000	0.0000		1.000	0.000	385.80	0.5739	0.9117	1.150	1.257	0.178
444.79	0.0082	0.0669	1.608	0.998	0.002	384.48	0.6114	0.9204	1.130	1.302	0.177
441.09	0.0208	0.1568	1.588	1.001	0.011	383.18	0.6479	0.9291	1.115	1.342	0.174
437.03	0.0357	0.2518	1.601	0.999	0.016	382.32	0.6810	0.9354	1.094	1.392	0.167
432.26	0.0547	0.3527	1.603	0.997	0.023	381.16	0.7285	0.9441	1.066	1.477	0.152
428.68	0.0722	0.4238	1.566	0.995	0.028	380.28	0.7635	0.9506	1.050	1.548	0.141
423.19	0.0998	0.5187	1.550	0.996	0.040	379.43	0.8002	0.9566	1.032	1.661	0.127
417.23	0.1383	0.6084	1.489	1.003	0.058	378.33	0.8427	0.9654	1.021	1.753	0.106
411.51	0.1803	0.6840	1.457	1.007	0.074	377.27	0.8839	0.9734	1.011	1.900	0.084
406.02	0.2298	0.7473	1.416	1.014	0.091	376.49	0.9143	0.9799	1.006	2.004	0.065
401.08	0.2811	0.7967	1.388	1.022	0.108	375.87	0.9382	0.9847	1.003	2.166	0.051
397.63	0.3242	0.8281	1.362	1.029	0.119	375.31	0.9578	0.9890	1.003	2.330	0.039
394.41	0.3707	0.8539	1.331	1.045	0.134	374.92	0.9734	0.9926	1.002	2.524	0.027
391.99	0.4155	0.8709	1.289	1.079	0.150	374.62	0.9839	0.9954	1.003	2.622	0.018
390.36	0.4598	0.8815	1.230	1.134	0.163	374.35	0.9934	0.9976	1.004	3.372	0.012
388.74	0.5001	0.8919	1.194	1.182	0.172	374.34	1.0000	1.0000	1.000		0.000
387.75	0.5249	0.8984	1.176	1.210	0.176						

<sup>a</sup>Uncertainties  $u$  are:  $u(T) = \pm 0.01$  K,  $u(p) = \pm 0.02$  kPa,  $u(x_1) = \pm 0.002$ , and  $u(y_1) = \pm 0.002$ .

being calculated  $k_r^{21}$  and  $k_q^{21}$  by a procedure already used.<sup>2,3</sup> The parameter  $k_r^{21}$  is the quotient of the van der Waals group volume parameters  $R_k$ , given by Bondi,<sup>32</sup> by the sum  $r_i = \sum_k v_k^{(i)} R_k$  weighted by the number of  $k$  type groups in the molecule  $i$ ,  $v_k^{(i)}$ . The parameter  $k_q^{21}$  is the quotient of  $q_i$  parameters,  $k_q = q_2/q_1$ , which are obtained from the weighted sum of the van der Waals group area parameters  $Q_k$  by  $q_i = \sum_k v_k^{(i)} Q_k$ . Now, the different properties are correlated to obtain the  $y_{ij}$  coefficients of eq 3. Table 7 shows the coefficients obtained in the regression of the experimental values of volumes and enthalpies

to an expression such as eq 3. A nonlinear regression procedure was followed using a software based in the simplex-method implemented in Matlab and minimizing the standard deviation of data,  $s(y^E)$ . Figures 2 and 3 represent, respectively, the functions obtained for the fits of  $v^E(x_1, T)$  and  $h^E(x_1, T)$ . Both in Figure 2 and in Table 7 (through the standard deviations) high values of  $s$  are observed in the  $v^E$  correlation curves, but these differences are smaller for the  $h^E$ . This is because of the difficulty to correlate the  $v^E$  at four temperatures with the same model and the presence of a sigmoidal



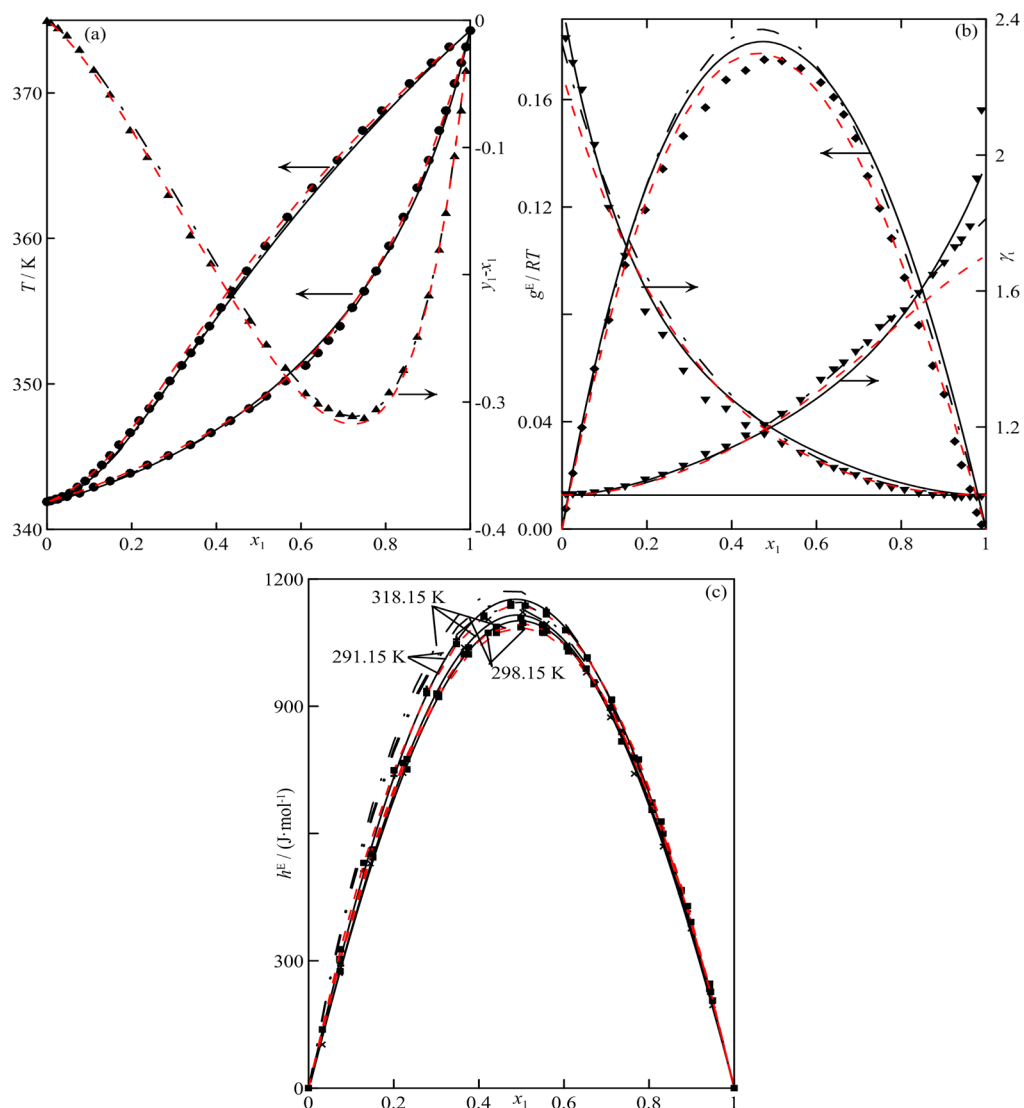
**Figure 4.** Plots of experimental values and curves obtained in the multiproperty correlation process (—, proposed model; red dashed line, NRTL; — — —, UNIFAC) for binary propyl ethanoate (1) + pentane (2). (a) iso- $p$  VLE, this work: ●,  $T$  vs  $x_1, y_1$ ; ▲,  $(y_1 - x_1)$  vs  $x_1$ . (b) iso- $p$  VLE, this work: ◆,  $g^E/RT$  vs  $x_1$ ; ▼,  $\gamma_i$  vs  $x_1$ . (c)  $h^E$  vs  $x_1$  at  $T = 291.15$  K (■) and  $T = 298.15$  K (×) (ref 4).

distribution of the points corresponding to the propyl ethanoate + pentane system at temperatures of (291.15 and 298.15) K. It was checked how the introduction of a variation in the  $k_v^{21}$  and  $k_h^{21}$  parameters with  $T$  in the regression process did not significantly change the final results.

Regarding the interpretation of the results of mixing properties, the systems studied present expansive effects in all cases,  $v^E > 0$ , also complying with  $(\partial v^E / \partial T)_p > 0$  in the range of temperatures used in this work. Although the enthalpies are found to obey the expression  $h^E > 0$ , variation of this property with temperature presents an inversion of the slope  $(\partial h^E / \partial T)_p$ , which goes from negative, in systems with  $n > 6$  in the interval (291.15 to 298.15) K, to positive in the interval (298.15 to 318.15) K. However, this change is not as pronounced in systems with  $n \leq 6$ . This behavior confirms the details of the structural model presented in previous works,<sup>3–5</sup> explaining the expansive and endothermic effects of the experimentation and the increase in excess quantities with increasing alkane chain length. By contrast, if net values of the properties  $v^E$  and  $h^E$  of the mixtures with different ethanoates

are compared a slight increase in the permanent dipolar moment is observed  $\mu \cdot 10^{30} / (\text{C} \cdot \text{m})$  associated with the COO-group (5.60 for methyl, 5.90 for ethyl, and 5.97 for propyl) that gives rise to an increase in the dipole–dipole attractions, both in the pure component and in the mixture, but less pronounced in the latter due to the greater distance between the dipoles. If this were the only effect, the mixing process would raise the endothermicity and expansivity with increasing alkanolic chain length of the ethanoate. However, experimentally, we find that the opposite occurs, indicating that the effect of  $\mu$  is smaller than the effect dominating these types of mixtures, such as the molecular size of the ethanoates, in other words, due to the increase in nonpolar interactions.

It is important to highlight the aforementioned effect of temperature on  $h^E$  since variations in  $h^E = \varphi(T)$  present local minima where  $c_p^E = 0$ . The literature<sup>9</sup> contains data for systems of propyl ethanoate +  $C_7$ , +  $C_{10}$ , presenting in both cases a so-called “omega effect” of the curves, although in the former system, the representation of  $c_p^E = \vartheta(x)$  cuts the abscissa at two points. In the



**Figure 5.** Plots of experimental values and curves obtained in the multiproperty correlation process (—, proposed model; red dashed line, NRTL; — — —, UNIFAC) of the binary propyl ethanoate (1) + hexane (2). (a) iso- $p$  VLE, this work:  $\bullet$ ,  $T$  vs  $x_1, y_1$ ;  $\blacktriangle$ ,  $(y_1 - x_1)$  vs  $x_1$ . (b) iso- $p$  VLE, this work:  $\blacklozenge$ ,  $g^E/RT$  vs  $x_1$ ;  $\blacktriangledown$ ,  $\gamma_i$  vs  $x_1$ . (c)  $h^E$  vs  $x_1$  this work: at  $T = 291.15$  K ( $\blacksquare$ ), at  $T = 298.15$  K ( $\times$ ), at  $T = 318.15$  K ( $+$ ).

second mixture mentioned above, the “omega curve” appears in the negative region, indicating that the minimum of the function  $h^E = h^E(T)$  should be found at temperatures higher than 298.15 K, which does occur with the data presented in Table 4. This unusual behavior of some esters in solution is due to the change in their dipolar moments with temperature,<sup>33</sup> which is reflected in their thermal capacities. Pure esters present a conformational equilibrium between the *s-trans* and *s-cis* forms, but any change, such as the presence of foreign molecules, would also produce a change in the electrical dipolar moment,<sup>34</sup> caused by a shift in this equilibrium. Another consequence is that the curves  $c_p^E = \vartheta(x)$  are  $\omega$ -shaped, which, in fact, corresponds to a superposition of two “v-shaped” curves, each corresponding to a dominant conformation. Evidently, at low values for the molar fraction of the ester the dominant *s-trans* shaped curve appears, while at high values of  $x$  the *s-cis* shaped curve dominates. The two “v-shaped” curves form the central maximum of these types of representations.

**VLE Data.** The direct experimental values obtained for isobaric VLE values at  $(101.32 \pm 0.02)$  kPa for the six binaries  $\text{H}_3\text{CCOOC}_3\text{H}_7$  (1) +  $\text{C}_n\text{H}_{2n+2}$  (2) ( $n = 5$  to 10) are recorded

in Table 8 and represented graphically in Figures 4a to 9a. A comparison of the experimental values obtained in this work with those from another previously published,<sup>6</sup> is carried out by means of the representations of  $T$  vs  $x_1, y_1$  and  $(y_1 - x_1)$  vs  $x_1$  for the binaries of propyl ethanoate with heptane and nonane. These are shown in Figure 6a and 8a, respectively, showing an acceptable agreement between them. There was some discrepancy between the coordinates ( $x_{az}, T_{az}/\text{K}$ ) found for the azeotropic point of the binary with  $n = 7$ , of (0.445, 367.05), (0.423, 366.99);<sup>35</sup> the mixture with  $n = 8$  produces an azeotropic point at (0.973, 374.31) although no data have been found in the literature for comparison. Figure 1b represents the azeotropic points obtained in isobaric and isothermic conditions for the propyl ethanoate + heptane mixture, using reduced coordinates. The distribution of the azeotropic points for this mixture has enabled a correlation to be achieved using an analogous equation to Antoine’s equation, the expression of which appears at the footnote of Figure 1.

The coefficients of activity  $\gamma_i$  of each component in the mixtures were calculated by considering the nonideality of the

vapor phase and determined by the expression:

$$\ln \gamma_i = \ln \left[ \frac{y_i p}{x_i p_i^o} \right] + \left[ \frac{(B_{ii} - v_i^o)(p - p_i^o)}{RT} \right] + \left[ \frac{p \delta_{12}(1 - y_i)^2}{RT} \right] \quad (7)$$

where the vapor pressures,  $p_i^o$ , are obtained from Antoine's equation with the coefficients from Table 4 for the ester and those published in previous works<sup>3,36</sup> for the alkanes. The molar volumes  $v_i^o$  in saturation conditions were estimated using a modified version of Rackett's equation, using the values of  $Z_{RA}$  given by Spencer and Danner.<sup>37</sup> The second virial coefficients for the pure  $B_{ii}$  compounds and for the mixtures  $B_{12}$  were estimated with the expressions proposed by Tsonopoulos,<sup>38</sup> which are used to calculate the parameter  $\delta_{12} = 2B_{12} - B_{11} - B_{22}$ . The values calculated with eq 7 are presented in Table 8, together with the corresponding to the adimensional Gibbs function  $g^E/RT = \sum x_i \ln \gamma_i$  and are represented graphically in Figures 4b to 9b for the six systems studied. Compliance with the global condition

proposed by Fredenslund et al.<sup>39</sup> for the consistency of VLE data was verified previously. Activity coefficients for the mixtures reveal the degree of interaction among the components present, showing deviation from ideality of the liquid phase. Propyl ethanoate (1) + alkane (2) systems present a quasi-regular variation in the  $\gamma_{ij}$  and  $\gamma_2$  increases with alkane chain length while the  $\gamma_1$  decreases with the diminishing relative contact areas of the aliphatic portions. For the propyl ethanoate (1) + nonane (2) system there is a difference between the variation in the  $\gamma_1$  and those presented in a previous work,<sup>6</sup> which is not observed in the mixture with heptane, possibly due to the greater influence of the vapor pressures at higher temperatures corresponding to nonane rather than those of the ester; this is highlighted in section corresponding to vapor pressures, with reference to Figure 1a.

## ■ CORRELATION AND PREDICTION OF PROPERTIES FOR PROPYL ETHANOATE + ALKANE MIXTURES

**Correlation.** For the mathematical treatment of the properties of each of the binary systems a multiproperty correlation procedure was employed using two models, the principles of which are described below:

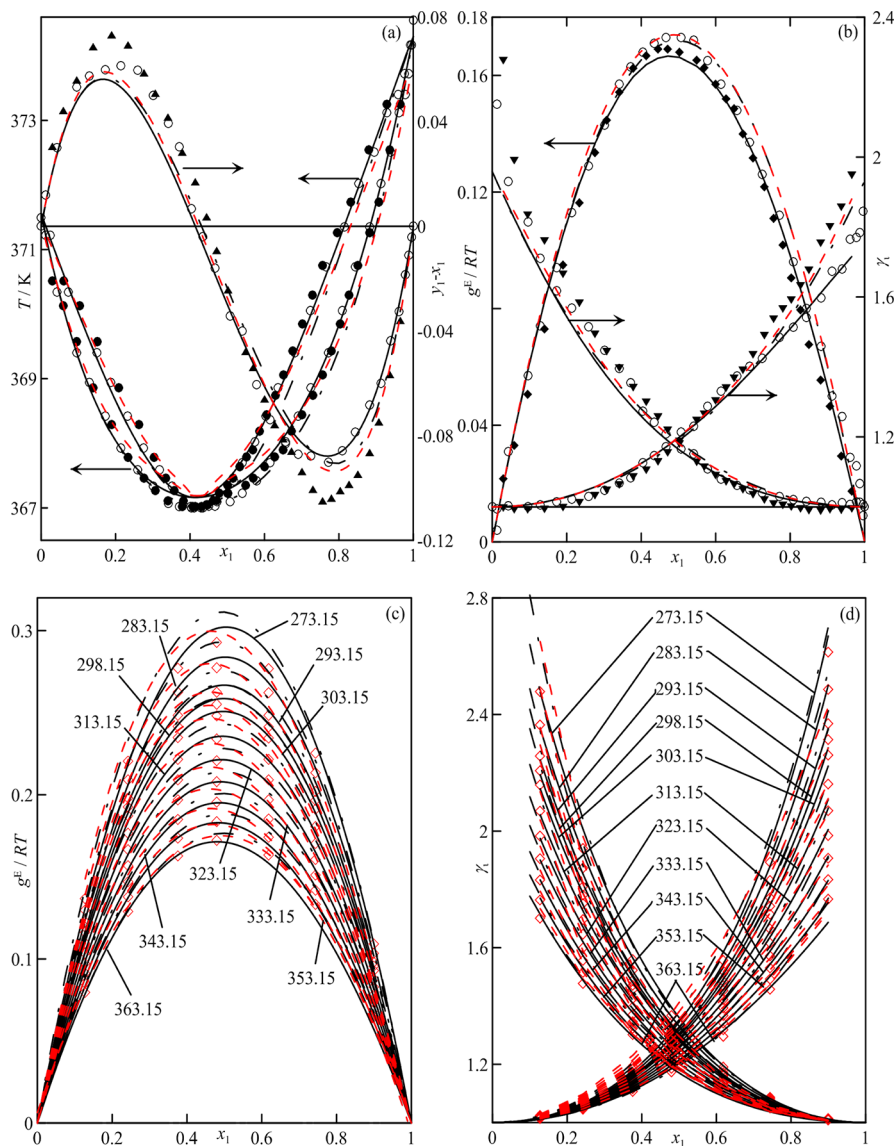
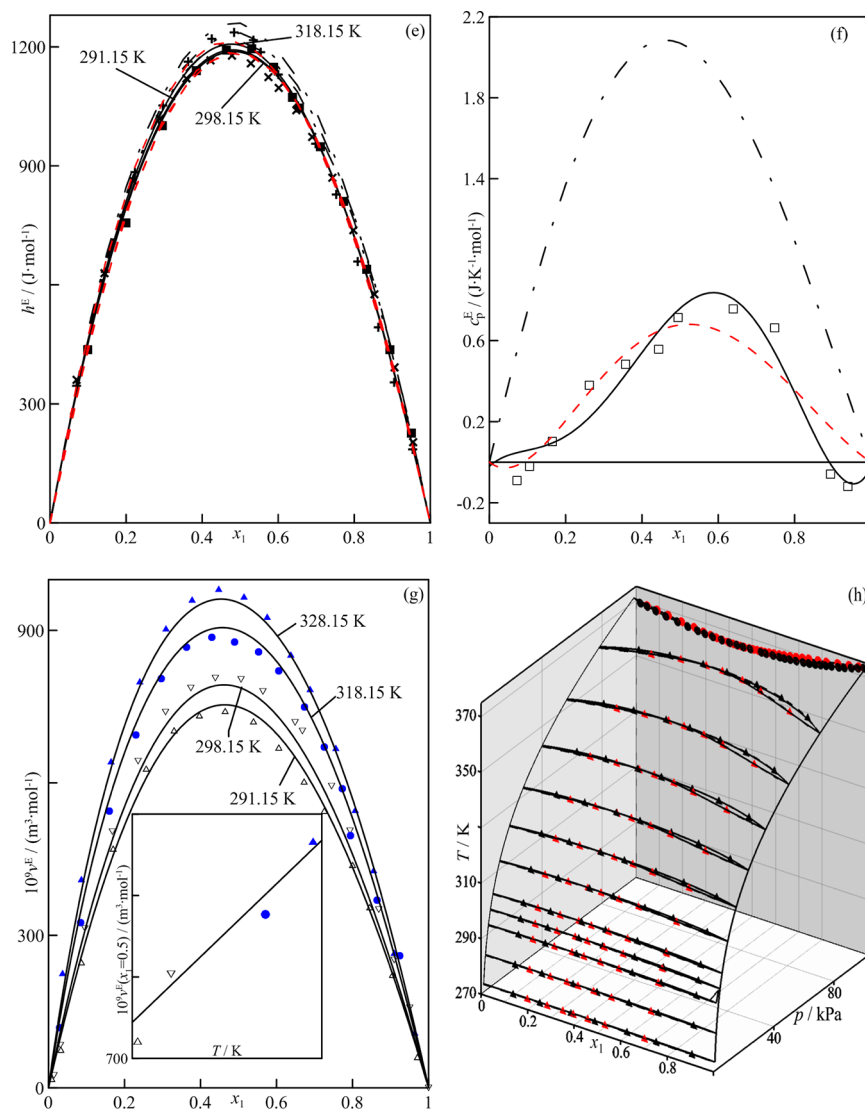


Figure 6. continued



**Figure 6.** Plots of experimental values and curves obtained in the multiproperty correlation process (—, proposed model; red dashed line, NRTL; — —, UNIFAC) of the binary propyl ethanoate (1) + heptane (2). (a) iso- $p$  VLE, this work:  $\bullet$ ,  $T$  vs  $x_1, y_1$ ;  $\blacktriangle$ ,  $(y_1 - x_1)$  vs  $x_1$ ;  $\circ$ , from ref 6. (b) iso- $p$  VLE, this work:  $\blacklozenge$ ,  $g^E/RT$  vs  $x_1$ ;  $\blacktriangledown$ ,  $\gamma_i$  vs  $x_1$ ;  $\circ$ , from ref 6. (c) iso- $T$  VLE, red  $\blacklozenge$ ,  $g^E/RT$  vs  $x_1$  from ref 13. (d) iso- $T$  VLE, red  $\blacklozenge$ ,  $\gamma_i$  vs  $x_1$  from ref 13. (e)  $h^E$  vs  $x_1$ , this work: at  $T = 291.15$  K ( $\blacksquare$ ), at  $T = 298.15$  K ( $\times$ ) from ref 4, at  $T = 318.15$  K ( $+$ ) from ref 5. (f)  $c_p^E$ -values ( $\square$ ) at  $T = 298.15$  K from ref 9. (g)  $v^E$  vs  $x_1$ , this work: at  $T = 291.15$  K ( $\triangle$ ), at  $T = 298.15$  K ( $\nabla$ ), at  $T = 318.15$  K (blue  $\bullet$ ), at  $T = 328.15$  K (blue  $\blacktriangle$ ); inset shows the equimolar  $v^E(T)$  experimental values and the corresponding straight-line estimated by the proposed model. (h) 3D-representation of iso- $p$  VLE experimental values (circle) in this work and iso- $T$  VLE from literature (triangle) and correlation curves using the proposed model for binary propyl ethanoate + heptane.

I. A polynomial model implemented over the excess Gibbs function  $g^E = g^E(x_1, p, T)$ , with a similar formula to eq 3. This procedure has already been described and used in previous works,<sup>3,15,16</sup> so only a summary of the equations used are presented here:

The main model:

$$g^E = z_1(1 - z_1)(g_0 + g_1z_1 + g_2z_1^2) \quad (8)$$

Expression for the coefficients:

$$g_i(p, T) = G_{i1} + G_{i2}p^2 + G_{i3}pT + G_{i4}/T + G_{i5}T^2 \quad (9)$$

Expression for  $z_1$  of Gibbs function:

$$z_1 = x_1/(x_1 + k_g^{21}x_2) \quad (10)$$

Expression for  $h^E$ :

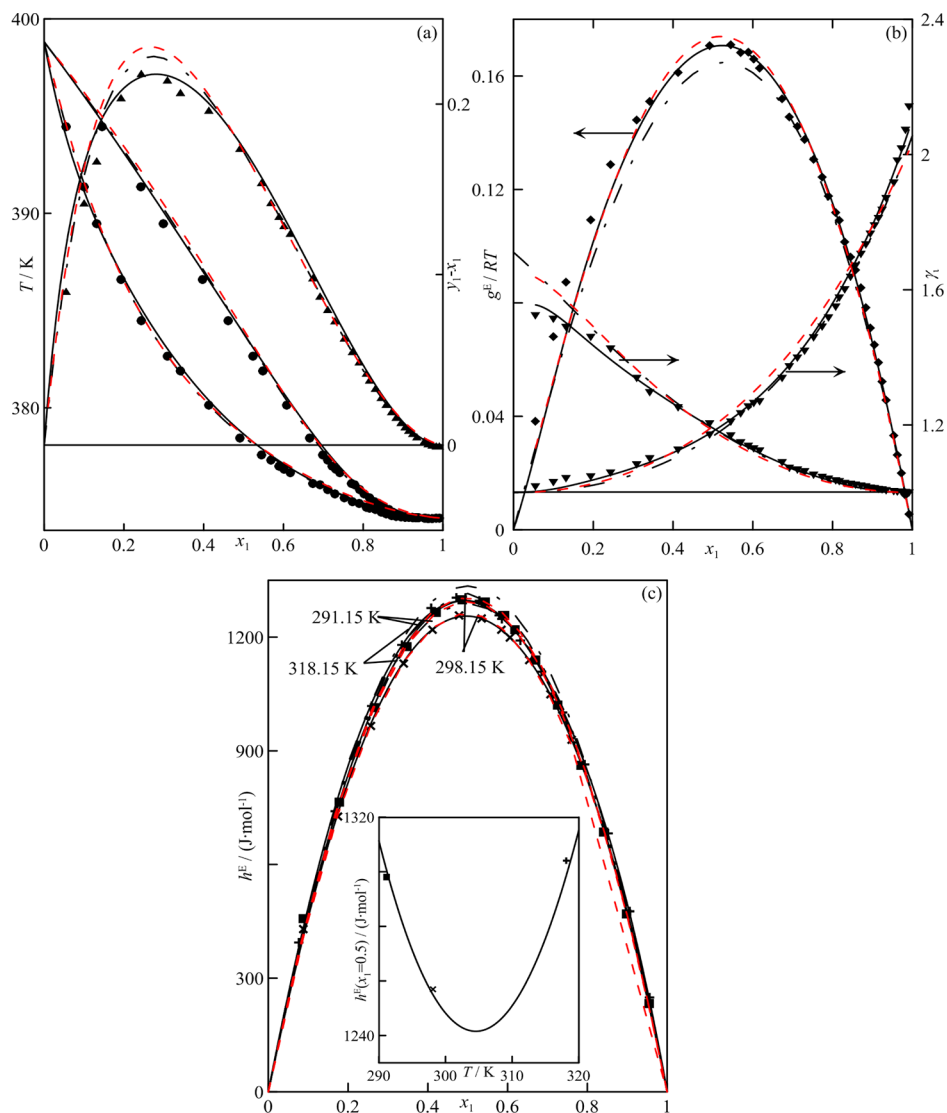
$$h^E = g^E - T \left( \frac{\partial g^E}{\partial T} \right)_p = z_1(1 - z_1) \sum_{i=0}^2 \left[ g_i - T \left( \frac{\partial g_i}{\partial T} \right)_p \right] z_1^i \quad (11)$$

Expression for  $c_p^E$ :

$$c_p^E = \left( \frac{\partial h^E}{\partial T} \right)_p = -z_1(1 - z_1)T \sum_{i=0}^2 \left( \frac{\partial^2 g_i}{\partial T^2} \right) z_1^i \quad (12)$$

Expression for  $v^E$ :

$$v^E = \left( \frac{\partial g^E}{\partial p} \right)_T = z_1(1 - z_1) \sum_{i=0}^2 \left( \frac{\partial g_i}{\partial p} \right)_T z_1^i \quad (13)$$



**Figure 7.** Plots of experimental values and curves obtained in the multiproperty correlation process (—, proposed model; red dashed line, NRTL; —·—, UNIFAC) of the binary propyl ethanoate (1) + octane (2). (a) iso-*p* VLE, this work: ●,  $T$  vs  $x_1, y_1$ ; ▲,  $(y_1 - x_1)$  vs  $x_1$ . (b) iso-*p* VLE, this work: ◆,  $g^E/RT$  vs  $x_1$ ; ▼,  $\gamma_i$  vs  $x_1$ . (c)  $h^E$  vs  $x_1$  this work: at  $T = 291.15$  K (■), at  $T = 298.15$  K (×), at  $T = 318.15$  K (+); inset shows the variation of equimolar  $h^E(T)$  as a function of  $T$  and the corresponding curve obtained by the proposed model.

For each of the properties a value is determined for the corresponding  $k$  parameter ( $k_c^{21}, k_h^{21}, k_c^{12}, k_v^{21}$ ) independent in each case according to the particular expression for the active fraction of the corresponding property, eq 10. They are considered as adjustable parameters in the regression procedure.

Equations 8 and 11 to 13 can be defined using a multiobjective optimization algorithm to locate the set of coefficients,  $g_p$  that give the best fit for the set of excess properties. A regression method has been employed for nonlinear functions, implemented in Matlab, generating an objective function (OF) where a weighted standard deviation is considered for each of the properties in the correlation procedure.

$$\text{OF} = \sum_1^n c_s (y^E) = \sum_1^n c_i \left[ \sum_1^N (y_{i,\text{exp}}^E - y_{i,\text{cal}}^E)^2 / (N - 1) \right]^{1/2} \quad (14)$$

where  $s(y^E)$  represents the standard deviations corresponding to each of the properties  $y^E = \text{VLE (iso-}p, \text{iso-}T), h^E, v^E, c_p^E$  considered in the fitting procedure,  $N$  is the number of experimental points

for each property, and  $n$  the number of different properties that are correlated. The coefficients “ $c$ ” are correction-parameters for the different quantities, which permit these to be modulated (into an interval) to obtain the best value for OF.

II. The NRTL model,<sup>17</sup> one of the most used for treatment of the thermodynamic properties of solutions, is also used here to validate the application indicated. The basic expression of the model on the Gibbs function is:

$$g^E/RT = x_1 x_2 \left[ \frac{G_{12} \tau_{12}}{G_{12} x_1 + x_2} + \frac{G_{21} \tau_{21}}{x_1 + G_{21} x_2} \right] \quad (15)$$

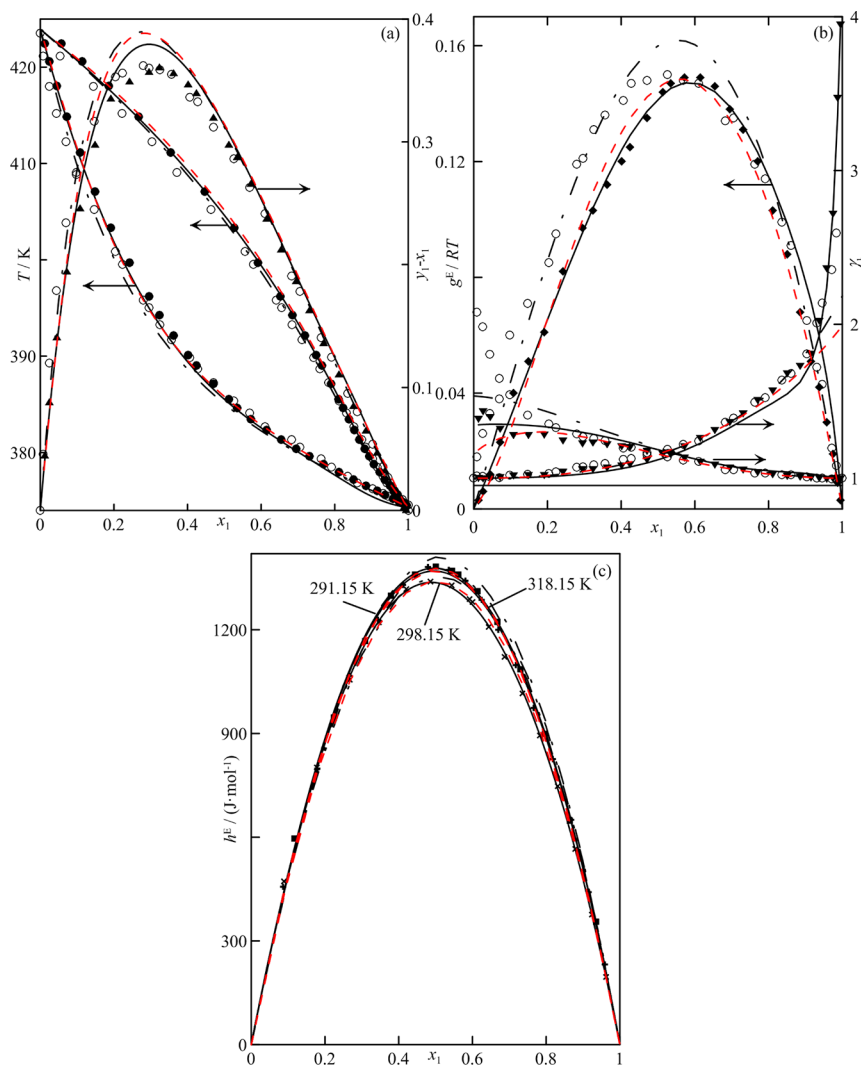
with

$$G_{ij} = \exp(-\alpha \tau_{ij}) \quad (16)$$

but with

$$\tau_{ij} = \Delta g_{ij0} + \frac{\Delta g_{ij1}}{T} + \Delta g_{ij2} \log T + \Delta g_{ij3} T \quad (17)$$





**Figure 8.** Plots of experimental values and curves obtained in the multiproperty correlation process (—, proposed model; red dashed line, NRTL; — — —, UNIFAC) of the binary propyl ethanoate (1) + nonane (2). (a) iso-*p* VLE, this work: ●,  $T$  vs  $x_1, y_1$ ; ▲,  $(y_1 - x_1)$  vs  $x_1$ ; ○, from ref 6. (b) iso-*p* VLE, this work: ◆,  $g^E/RT$  vs  $x_1$ ; ▼,  $\gamma_1$  vs  $x_1$ ; ○, from ref 6. (c)  $h^E$  vs  $x_1$  this work: at  $T = 291.15$  K (■); at  $T = 298.15$  K (×) from ref 4, at  $T = 318.15$  K (+) from ref 5.

being now  $\Delta g_{ijk}$  the parameters of extended NRTL equation.

$$h^E = R x_1 x_2 \left[ \frac{\tau'_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{x_1 \tau'_{21} G'_{21}}{(x_1 + x_2 G_{21})^2} + \frac{\tau'_{12} G_{12}}{x_1 G_{12} + x_2} + \frac{x_2 \tau'_{12} G'_{12}}{(x_1 G_{12} + x_2)^2} \right] \quad (18)$$

$$\tau'_{ij} = \frac{d\tau_{ij}}{d(1/T)} \quad \text{and} \quad G'_{ij} = \frac{dG_{ij}}{d(1/T)} \quad (19)$$

Equation 17 is the extended form of another expression previously presented in the literature by Ko et al.,<sup>40</sup> since the original, simpler one does not allow an adequate representation of Gibbs function  $g^E$  over a broad temperature range. From eq 18 the one corresponding to  $c_p^E = (\partial h^E / \partial T)_{p,x}$  is obtained,

$$c_p^E/RT = -x_1 x_2 \left[ 2 \frac{\partial}{\partial T} \left( \frac{G_{12} \tau_{12}}{G_{12} x_1 + x_2} + \frac{G_{21} \tau_{21}}{x_1 + G_{21} x_2} \right) + T \frac{\partial^2}{\partial T^2} \left( \frac{G_{12} \tau_{12}}{G_{12} x_1 + x_2} + \frac{G_{21} \tau_{21}}{x_1 + G_{21} x_2} \right) \right] \quad (20)$$

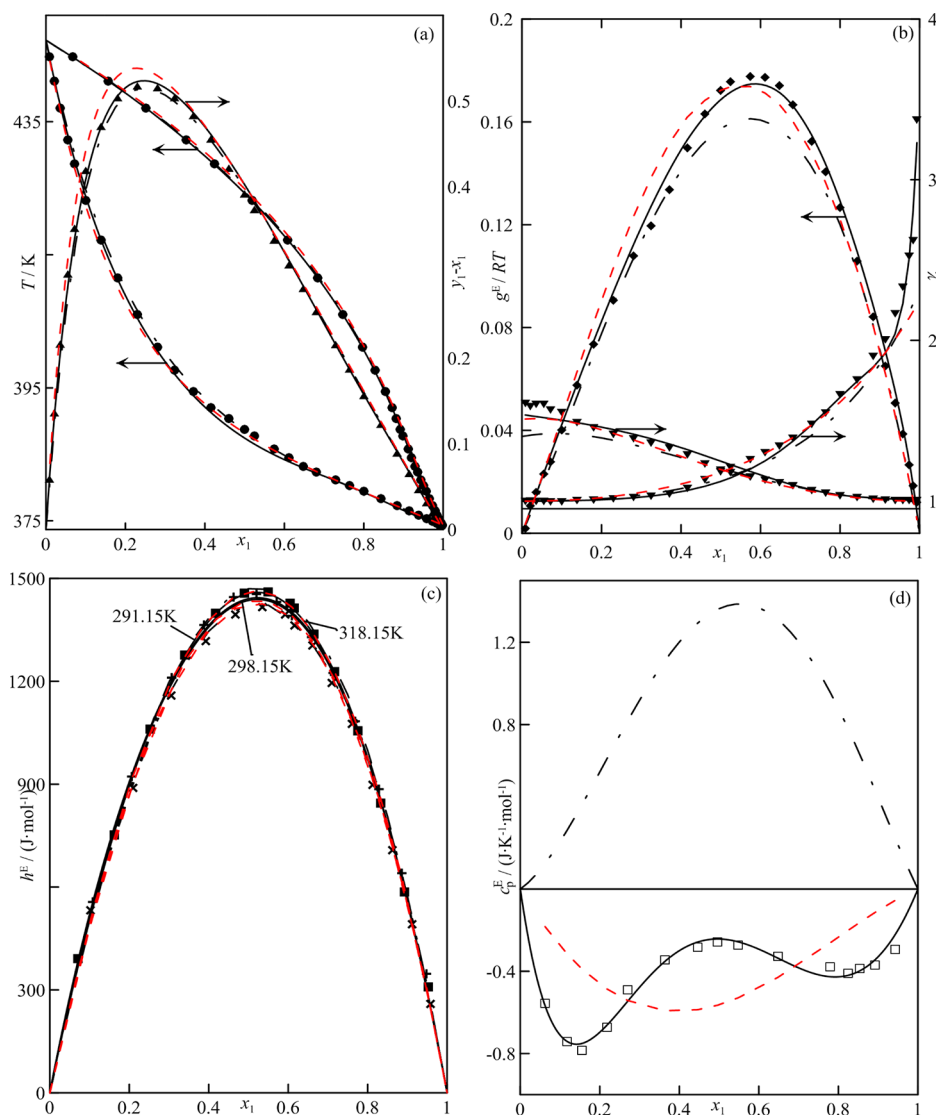
or an alternative form more condensed:

$$c_p^E/RT = \left[ 2(h^E/RT) - T \frac{\partial(h^E/RT)}{\partial T} \right] \quad (21)$$

Hence, in this model nine parameters can be determined to optimize the correlation, eight  $\Delta g_{ijk}$  included in eq 17 and the nonrandomness parameter  $\alpha$ . The correlation procedure is the same as the one recorded in part I, using the same (OF) expressed by eq 14.

**Prediction.** The version by Gmehling et al.<sup>18</sup> of the UNIFAC method was used to estimate the mixing properties of the six saturated hydrocarbons with propyl ethanoate, and the results for  $g^E$ ,  $\gamma$ ,  $h^E$ ,  $T$ , and for  $(y_1 - x_1)$ , vs  $x_1$  are shown in Figures 4 to 9 which also include the estimations of  $c_p^E$  vs  $x_1$  for the systems with heptanes and decane.

The coefficients obtained for the two models described in detail in the previous section for the correlation of six systems are recorded in Table 7. Owing to the variable availability of experimental data for each of the systems studied in this work, the results obtained for each binary system are discussed in detail in the following paragraphs.



**Figure 9.** Plots of experimental values and curves obtained in the multiproperty correlation process (—, proposed model; red dashed line, NRTL; — · —, UNIFAC) of the binary propyl ethanoate (1) + decane (2). (a) iso- $p$  VLE, this work: ●,  $T$  vs  $x_1, y_1$ ; ▲,  $(y_1 - x_1)$  vs  $x_1$ . (b) iso- $p$  VLE, this work: ◆,  $g^E/RT$  vs  $x_1$ ; ▼,  $\gamma_i$  vs  $x_1$ . (c)  $h^E$  vs  $x_1$  this work: at  $T = 291.15$  K (■); at  $T = 298.15$  K (×); at  $T = 318.15$  K (+). (d)  $c_p^E$ -values (□) at  $T = 298.15$  K from ref 9.

**Propyl Ethanoate + Pentane, + Hexane, + Octane, + Nonane.** For this set of systems  $\text{H}_3\text{CCOOC}_3\text{H}_7$  (1) +  $\text{C}_n\text{H}_{2n+2}$  (2) ( $n = 5, 6, 8, 9$ ) experimental VLE data iso- $p$ ,  $p = 101.32$  kPa, and the  $h^E$  are only available at three temperatures (indicated previously). Correlations for the thermodynamic properties,  $\gamma_i$  and  $g^E$ , for these systems are shown in Figures 4b to 9b, and the quality of fit is acceptable in all cases. The model adequately reproduces the excess enthalpies, even with the inversion that appears with changing temperature, which produces a local minimum for the function  $h^E = \varphi(T)$ . The model was also used to reproduce equilibrium quantities ( $T$ ,  $x_1$ ,  $y_1$ ) and to validate its use. Almost all representations obtained were good except for the mixture containing nonane, which was considered to be acceptable; for this mixture the mole fractions obtained of the vapor phase  $y_1$  were higher than those obtained in the real experimentation; see Figure 8a.

The NRTL correlation of the four systems considered in this section is acceptable, although quantitatively inferior to that of the proposed model, eqs 8 to 13. The  $h^E$  values present an adequate fit, even showing the inversion of the enthalpy with temperature in cases  $n = 8$  and 9. The  $\alpha$ -values were obtained in the same correlation process as an additional parameter to get the

best fit. In some cases the optimum  $\alpha$ -values obtained are very small,  $\ll 0.01$ , so the exponential of eq 16 has less influence in the model. Hence, eq 15 and its derivatives are transformed into polynomial expressions.

For these mixtures, the UNIFAC method slightly overestimates  $g^E$  values, and reproductions of the quantities  $T$ ,  $x_1$ ,  $y_1$  are similar to those obtained with the correlation model employed, and the previous observations can also apply here. The method determines, at least qualitatively, values of  $h^E$  reasonably close to experimental ones but does not reproduce the real change in this quantity with temperature. In other words, it does not show the  $h^E$  inversion produced for these systems in the interval (291 to 298) K. Quantitatively the average estimation is less than 5 % for that property. The method does not estimate the experimental azeotropic point obtained for the (propyl ethanoate + octane) system.

**Propyl Ethanoate + Heptane.** This binary system has been studied by other authors, and the literature provides (iso- $p$ )<sup>6</sup> and (iso- $T$ )<sup>13</sup> VLE data at different temperatures, and even values of  $c_p^E$ .<sup>9</sup> The model proposed, eqs 8 to 13, offers a good correlation of the different properties; see Figure 6a–h. In this case, for the

**Table 9. Parameters for eqs 8 and 15 Obtained in the Multiproperty Correlation of Several Properties (iso- $p$  and iso- $T$  VLE Data,  $10^9 v^E(x_i, T)$ ,  $h^E(x_i, T)$ ,  $c_p^E(x_i)$ , for Propyl Ethanoate (1) + an Alkane (2) Mixtures and Standard Deviations  $s$  Calculated for Each of the Quantities**

propyl ethanoate +	eqs 8 to 13			NRTL		
	$i = 0$	$i = 1$	$i = 2$	$i$	$\tau_{12i}$	$\tau_{21i}$
pentane						
$g_{i1}$	$-2.362 \cdot 10^5$	$-4.332 \cdot 10^4$	$8.193 \cdot 10^4$	1	$-5.176 \cdot 10^1$	$2.373 \cdot 10^3$
$g_{i2}$	$-1.840 \cdot 10^1$	$-4.731 \cdot 10^1$	$5.341 \cdot 10^1$	2	$4.764 \cdot 10^3$	$-7.243 \cdot 10^4$
$g_{i3}$	$1.488 \cdot 10^1$	$1.913 \cdot 10^1$	$-2.407 \cdot 10^1$	3	$4.257 \cdot 10^0$	$-4.008 \cdot 10^2$
$g_{i4}$	$4.029 \cdot 10^7$	$4.770 \cdot 10^7$	$-5.239 \cdot 10^7$	4	$3.576 \cdot 10^{-2}$	$5.263 \cdot 10^{-1}$
$g_{i5}$	$-1.769 \cdot 10^0$	$-2.358 \cdot 10^0$	$3.088 \cdot 10^0$	$\alpha$	0.259	
$k_g^{21}$	0.534		0.013	$\leftarrow s(g^E/RT)$	$\rightarrow$	0.013
$k_h^{21}$	0.369		0.177	$\leftarrow s(\gamma_i)$	$\rightarrow$	0.251
$k_v^{21}$			26	$\leftarrow s(h^E)$	$\rightarrow$	41
hexane						
$g_{i1}$	$4.898 \cdot 10^3$	$-4.538 \cdot 10^3$	$3.964 \cdot 10^3$	1	$-1.752 \cdot 10^2$	$1.372 \cdot 10^2$
$g_{i2}$	$-3.825 \cdot 10^{-5}$	$7.147 \cdot 10^{-5}$	$-7.703 \cdot 10^{-5}$	2	$6.275 \cdot 10^3$	$-5.051 \cdot 10^3$
$g_{i3}$	$3.244 \cdot 10^{-5}$	$-4.999 \cdot 10^{-5}$	$6.109 \cdot 10^{-5}$	3	$2.864 \cdot 10^1$	$-2.174 \cdot 10^1$
$g_{i4}$	$-4.563 \cdot 10^5$	$1.199 \cdot 10^6$	$-7.500 \cdot 10^5$	4	$-3.443 \cdot 10^{-2}$	$1.994 \cdot 10^{-2}$
$g_{i5}$	$-9.191 \cdot 10^{-3}$	$-2.881 \cdot 10^{-3}$	$-3.238 \cdot 10^{-3}$	$\alpha$	0.040	
$k_g^{21}$	0.978		0.007	$\leftarrow s(g^E/RT)$	$\rightarrow$	0.004
$k_h^{21}$	0.706		0.012	$\leftarrow s(\gamma_i)$	$\rightarrow$	0.152
$k_v^{21}$	0.413		29	$\leftarrow s(h^E)$	$\rightarrow$	41
heptane						
$g_{i1}$	$1.921 \cdot 10^3$	$3.601 \cdot 10^3$	$-2.914 \cdot 10^3$	1	$-4.286 \cdot 10^2$	$-4.069 \cdot 10^2$
$g_{i2}$	$-4.502 \cdot 10^{-5}$	$9.577 \cdot 10^{-5}$	$-8.485 \cdot 10^{-5}$	2	$1.492 \cdot 10^4$	$5.394 \cdot 10^3$
$g_{i3}$	$3.873 \cdot 10^{-5}$	$-6.140 \cdot 10^{-5}$	$5.957 \cdot 10^{-5}$	3	$6.986 \cdot 10^1$	$7.983 \cdot 10^1$
$g_{i4}$	$1.341 \cdot 10^5$	$-4.455 \cdot 10^5$	$8.004 \cdot 10^5$	4	$-5.857 \cdot 10^{-2}$	$-2.259 \cdot 10^{-1}$
$g_{i5}$	$-4.830 \cdot 10^{-3}$	$-1.147 \cdot 10^{-2}$	$4.435 \cdot 10^{-3}$	$\alpha$	-0.112	
$k_g^{21}$	0.780	$s(g^E/RT)$	0.004	$\leftarrow s(g^E/RT)$	$\rightarrow$	0.010
$k_h^{21}$	0.6200		0.103	$\leftarrow s(\gamma_i)$	$\rightarrow$	0.118
$k_v^{21}$	0.6570		55	$\leftarrow s(h^E)$	$\rightarrow$	34
$k_c^{21}$	1.9314		75	$\leftarrow s(v^E)$	$\rightarrow$	
			0.06	$\leftarrow s(c_p^E)$	$\rightarrow$	0.11
octane						
$g_{i1}$	$-1.858 \cdot 10^5$	$6.624 \cdot 10^4$	$1.918 \cdot 10^4$	1	$-4.759 \cdot 10^2$	$-3.451 \cdot 10^{-1}$
$g_{i2}$	$-4.938 \cdot 10^0$	$1.573 \cdot 10^1$	$1.631 \cdot 10^1$	2	$-2.962 \cdot 10^4$	$3.543 \cdot 10^1$
$g_{i3}$	$7.857 \cdot 10^0$	$-7.783 \cdot 10^0$	$-5.642 \cdot 10^0$	3	$3.802 \cdot 10^1$	$4.251 \cdot 10^4$
$g_{i4}$	$2.462 \cdot 10^7$	$-2.317 \cdot 10^7$	$-1.938 \cdot 10^7$	4	$2.231 \cdot 10^{-1}$	$3.895 \cdot 10^1$
$g_{i5}$	$-8.911 \cdot 10^{-1}$	$9.085 \cdot 10^{-1}$	$5.871 \cdot 10^{-1}$	$\alpha$	$1.736 \cdot 10^{-5}$	
$k_g^{21}$	0.674		0.005	$\leftarrow s(g^E/RT)$	$\rightarrow$	0.006
$k_h^{21}$	1.561		0.029	$\leftarrow s(\gamma_i)$	$\rightarrow$	0.071
$k_v^{21}$			25	$\leftarrow s(h^E)$	$\rightarrow$	20
nonane						
$g_{i1}$	$-1.135 \cdot 10^4$	$-1.081 \cdot 10^5$	$-4.588 \cdot 10^4$	1	$-5.010 \cdot 10^2$	$-3.139 \cdot 10^{-1}$
$g_{i2}$	$-3.064 \cdot 10^0$	$-4.009 \cdot 10^0$	$4.626 \cdot 10^0$	2	$-3.400 \cdot 10^4$	$7.848 \cdot 10^1$
$g_{i3}$	$1.546 \cdot 10^0$	$4.610 \cdot 10^0$	$9.635 \cdot 10^{-2}$	3	$3.761 \cdot 10^1$	$4.585 \cdot 10^4$
$g_{i4}$	$5.190 \cdot 10^6$	$1.436 \cdot 10^7$	$1.576 \cdot 10^5$	4	$1.929 \cdot 10^{-1}$	$3.610 \cdot 10^1$
$g_{i5}$	$-1.823 \cdot 10^{-1}$	$-5.066 \cdot 10^{-1}$	$-8.435 \cdot 10^{-3}$	$\alpha$	$-7.3 \cdot 10^{-7}$	
$k_g^{21}$	2.955		0.008	$\leftarrow s(g^E/RT)$	$\rightarrow$	0.005
$k_h^{21}$	1.511		0.095	$\leftarrow s(\gamma_i)$	$\rightarrow$	0.552
$k_v^{21}$			31	$\leftarrow s(h^E)$	$\rightarrow$	28
decane						
$g_{i1}$	$2.151 \cdot 10^4$	$-5.537 \cdot 10^4$	$3.504 \cdot 10^4$	1	$-6.894 \cdot 10^1$	$-1.521 \cdot 10^2$
$g_{i2}$	$-6.574 \cdot 10^{-1}$	$-3.917 \cdot 10^0$	$3.151 \cdot 10^0$	2	$1.133 \cdot 10^4$	$-3.525 \cdot 10^3$
$g_{i3}$	$-3.889 \cdot 10^{-1}$	$3.140 \cdot 10^0$	$-2.245 \cdot 10^0$	3	$-3.051 \cdot 10^0$	$3.957 \cdot 10^1$
$g_{i4}$	$-8.892 \cdot 10^5$	$9.064 \cdot 10^6$	$-5.880 \cdot 10^6$	4	$1.336 \cdot 10^{-1}$	$-1.760 \cdot 10^{-1}$
$g_{i5}$	$5.019 \cdot 10^{-2}$	$-3.953 \cdot 10^{-1}$	$2.693 \cdot 10^{-1}$	$\alpha$	-0.009	
$k_g^{21}$	3.238		0.003	$\leftarrow s(g^E/RT)$	$\rightarrow$	0.008
$k_h^{21}$	0.718		0.097	$\leftarrow s(\gamma_i)$	$\rightarrow$	0.279
$k_v^{21}$			59	$\leftarrow s(h^E)$	$\rightarrow$	40
$k_c^{21}$	0.737		0.03	$\leftarrow s(v^E)$	$\rightarrow$	
				$\leftarrow s(c_p^E)$	$\rightarrow$	0.29

simultaneous correlation of properties, in addition to those indicated here, the ones obtained experimentally for this work at isobaric conditions, VLE,  $h^E$  and  $v^E$  were also used. In Figure 6b we can observe that the correlation of the quantities of  $g^E$  and  $\gamma_i$  vs  $x_1$  are acceptable, although the representation gives values of  $\gamma_i$  vs  $x_1$  somewhat lower than those calculated from the experimentation. A difference is also found in the primary equilibrium data estimated  $T-x_1-y_1$ , but this barely influenced the reproduction of the azeotropic point (Figure 6a). The fit of the  $h^E$  values is good and show how the curve changes with temperature (Figure 6c). There is even an adequate representation of the irregular form ( $\omega$ -shaped) of the  $c_p^E$  data (Figure 6f). The experimental results generated<sup>13</sup> for the VLE iso- $T$  were introduced in the database used for the correlation process, together with the data of  $(x_1, v^E)$  presented in Table 3. Figure 6g shows an acceptable representation of the volumes at different temperatures, being the slope  $(\partial v^E/\partial T)_p < 0.07 \cdot 10^{-9} \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , very similar to that derived from the experimental values, as shown in the inset Figure 6g. After the model has been completely defined for a given binary system, an estimation can be made of the curves corresponding to the VLE, iso- $T$  and iso- $p$ , in the 3D-diagram ( $p-T-x_1, y_1$ ) and of  $p$  and  $T$  in the range available. The capacity of the model to reproduce the equilibrium data and data of the surface generated, and the mixing properties, is adequate (Figure 6h).

The fit with NRTL can be considered to be acceptable, and the observations made in the previous section also apply here. However, to elaborate on the properties only appearing in this system, the VLE-iso- $T$  are qualitatively well-reproduced (see Figure 6c,d), but the analysis of the  $g^E$  values shows quite a sharp deviation of the maximum toward mixtures with lower ester contents, which implies a curve with asymmetric morphology that does not correspond to the data. The  $c_p^E$  are not adequately reproduced with the NRTL model; the difficulty inherent to these data has already been mentioned previously. Moreover, NRTL and UNIFAC do not estimate excess molar volumes.

An acceptable estimation is only made with UNIFAC for the mixture of propyl ethanoate + heptane. The method predicts well the VLE iso- $T$  and iso- $p$ , although in both cases the values of  $\gamma_i$  and  $g^E/RT$  obtained are slightly higher than experimental ones. The change in  $h^E$  with temperature is not simulated by the model, which also loses the ability to represent the thermal capacities, as can be observed in Figure 6e,f. The UNIFAC model estimates an azeotropic point close to that obtained by experimentation.

**Propyl Ethanoate + Decane.** For this binary system, in addition to the data provided by this work,  $c_p^E$  data from the literature<sup>9</sup> have also been used in the multiproperty correlation process. Parameters of the model established by eqs 8 to 13 are shown in Table 9, together with the standard deviations obtained for each property, and on the whole, the results can be considered to be acceptable. Figure 9a–d reproduces the curves obtained in the correlation with a good degree of representation. In this case, a cutoff point for  $c_p^E$  with the abscissa is not observed (Figure 9d), so the minimum of the function  $h^E = h^E(T)$  must occur at temperatures higher than 298.15 K, which is consistent with the data presented in Table 4.

Similar observations to those made about the previous systems can be made about the fit of this system with NRTL. In general, the correlation appears to be acceptable although there are clear deviations in the fit of the VLE. The reproduction of thermal capacity does not produce the  $\omega$ -shaped pattern.

The UNIFAC method behaves in a similar way for this mixture as in previous cases, failing to estimate the function  $h^E = h^E(T)$

and generating an erroneous curve for  $c_p^E$ , as can be observed in Figure 9d.

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### Funding

The authors would like to thank the Ministry of Economy and Competitiveness for funding project CTQ2009-12482.

### Notes

The authors declare no competing financial interest.

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