

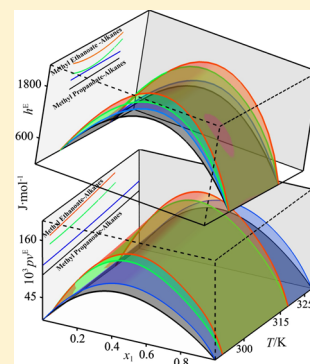
Improvements in the Experimentation and the Representation of Thermodynamic Properties (iso- p VLE and y^E) of Alkyl Propanoate + Alkane Binaries

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ABSTRACT: This paper presents the experimental measurements of isobaric vapor–liquid equilibria (iso- p VLE) and excess volumes (v^E) at several temperatures in the interval (288.15 to 328.15) K for six binary systems composed of two alkyl (methyl, ethyl) propanoates and three odd carbon alkanes (C5 to C9). The mixing processes were expansive, $v^E > 0$, with $(\delta v^E/\delta T)_p > 0$, and endothermic. The installation used to measure the iso- p VLE was improved by controlling three of the variables involved in the experimentation with a PC. Experimental iso-101.32 VLE data showed a positive consistency with Fredenslund's point-to-point method. Systems of methyl propanoate + heptane and ethyl propanoate + heptane presented azeotropes (x_{az}, T_{az}) at (0.844, 351.86) and (0.481, 366.61), respectively. Representations were obtained of $p v^E = \varphi(x, T)$ and $h^E = \varphi(x, T)$, using a model proposed previously [*Ind. Eng. Chem. Res.* **2010**, *49*, 406], and the behavior of the binary systems studied was interpreted. An adequate extended version of the same model was used to perform a stepwise correlation of the different properties according the following order $(x, T, c_p^E) \rightarrow (x, T, h^E) \rightarrow (x, T, g^E)$, positively valuing the multiproperty correlation. The paper conducts a comparison with the results obtained by applying the nonrandom two-liquid (NRTL) model, which were acceptable with the exception of the inadequate reproduction of values of the second derivative of the Gibbs function. The universal functional activity coefficient (UNIFAC) group contribution model did not give a satisfactory representation of the properties for the binaries of this work.



1. INTRODUCTION

In a previous work¹ of this series on ester + alkanes, experimental data were presented for several thermodynamic properties of the binary systems of alkyl (methyl, ethyl) butanoates with alkane (heptane, nonane), and a simultaneous correlation was performed for different properties (isobaric vapor–liquid equilibria, iso- p VLE, excess enthalpies h^E , and excess heat capacities c_p^E) with a polynomial model² and predictions with the universal functional activity coefficient (UNIFAC) method.³ The predictive method did not adequately reproduce the quantities of the first and second derivatives of the excess Gibbs function g^E . However, in systems with ethanoates⁴ and methanoates,^{5,6} where the model uses specific parameters for the carboxylate/methyl interactions, the prediction is acceptable for iso- p VLE and iso- T VLE and also for the first derivative h^E , but not the second c_p^E . In general, the representation appears to become poorer as the chain length of the compounds increases. There are limited data in the literature for propanoates and butanoates, and it is necessary to amplify the database for these systems to be able to verify their behavior and study their modeling in greater depth. In these cases it is essential to have basic knowledge of the solutions with saturated hydrocarbons. For this purpose, here the experimentation is conducted with substances with the following empirical notation: $H_3CCH_2COOC_uH_{2u+1}$ ($u = 1, 2$) + C_nH_{2n+2} ($n = 5, 7, 9$). Data for iso- p VLE and v^E have been determined at several

temperatures in the interval (288 to 328) K, since the h^{E7-9} and also iso- p VLE data for one of the binaries were presented previously.¹⁰ Data for the mixing properties, v^E and h^E , have been published in the literature^{11–14} for different conditions, and even for c_p^E .¹⁵

The combined correlation of the properties was conducted with a model proposed by the working team² together with the nonrandom two-liquid (NRTL) model,¹⁶ valuating the quality of the fit obtained with both models. It is interesting to know the utility of the UNIFAC group contribution method³ to reproduce the behavior of these solutions.

2. EXPERIMENTAL SECTION

2.1. Materials. The products used in this work were supplied by Aldrich, +99 % (w/w) purity, was verified by gas chromatography (GC). The propanoates gave slightly lower quality values than those indicated by the manufacturer, while values recorded for the alkanes were excellent. The esters were, therefore, distilled in a microdistillation apparatus in the presence of P_2O_5 , significantly improving their purity. A summarized description of these operations is given in Table 1. Moreover,

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Table 1. Description of the Materials Used

compound	source	initial mass fraction purity	physical treatment	final mass fraction purity	analysis method
pentane	Aldrich	> 0.99	none	> 0.99	GC
heptane	Aldrich	~ 0.99	none	~ 0.99	GC
nonane	Aldrich	~ 0.99	none	~ 0.99	GC
methyl propanoate	Aldrich	~ 0.978	distillation + molecular sieve	> 0.99	GC
ethyl propanoate	Aldrich	> 0.98	distillation + molecular sieve	> 0.99	GC
water			double distillation	conductance < 0.7 μ S	

Table 2. Properties of Pure Compounds:^a Densities and Refractive Indices Measured at Atmospheric Pressure

compound	water (ppm)	$T_{b,i}^{\circ}/\text{K}$		$\rho(298.15 \text{ K})/(\text{kg}\cdot\text{m}^{-3})$		$n_D(298.15 \text{ K})$	
		exptl	lit.	exptl	lit.	exptl	lit.
pentane	50	309.23	309.21 ^b	620.91	621.39 ^{b,d}	1.3547	1.35472 ^b
			309.22 ^d		621.35 ^c		309.30 ^c
			1.3545 ^c				
heptane	53	371.38	371.57 ^b	679.62	679.46 ^{b,d}	1.3853	1.3851 ^b
			371.51 ^d		679.48 ^c		1.3852 ^c
			371.56 ^c		679.51 ^e		
nonane	55	423.90	423.97 ^b	713.85	713.75 ^{b,d}	1.4032	1.4031 ^b
			423.94 ^c				1.4031 ^c
			423.95 ^d				
methyl propanoate	138	352.75	352.52 ^d	909.10	909.00 ^d	1.3743	1.3745 ^{c,e}
					909.01 ^e		
					909.07 ^f		
ethyl propanoate	143	372.09	372.25 ^b	884.19	884.0 ^b	1.3811	1.3814 ^b
					884.11 ^g		

^aUncertainties u are: $u(T) = \pm 0.02 \text{ K}$, $u(n) = \pm 0.0002$, and $u(\rho) = \pm 0.02 \text{ kg}\cdot\text{m}^{-3}$. ^bReference 16. ^cReference 4. ^dReference 17. ^eReference 15. ^fReference 18. ^gReference 19.

before use all products were submitted to a standard treatment commonly applied in our laboratory consisting in degasification with ultrasound for a few hours followed by storage for several days over a 0.3 nm SAFC molecular sieve to remove possible traces of moisture. The description of these operations appears in Table 1. All products were characterized by measuring properties, such as refractive indices n_D , and densities ρ at 298.15 K, and the normal boiling point $T_{b,i}^{\circ}$. A comparison of the experimental values with those from literature is shown in Table 2. This table also shows the final water content for the different products, measured with a Karl Fischer C80 coulometric titrator from Mettler.

2.2. Apparatus and Procedures. Vapor pressures of the pure compounds and iso- p VLE of the binaries in the study were measured in a small glass ebulliometer with recirculation of both phases.²⁰ To improve the experimentation a new pressurizing installation was designed by constructing stainless steel systems, with \varnothing 4 mm pipes and mini-tank regulators, as shown in Figure 1, which was previously tested to be hermetic. The apparatus used to control the pressure (DH-PPC2) was connected to a PC to capture the oscillations ($p \pm 0.02$) kPa throughout the experiment. For the temperature measuring device (Comarks-6800) with ($T \pm 0.01$) K, an electronic circuit was designed and constructed to translate the signal in BCD code to a parallel-port, also captured by PC. The signals corresponding to p/kPa and $t/^{\circ}\text{C}$ are recorded on the PC screen together with the power supplied to the ebulliometer w/watt and that required for heating in the two-phase zone (Figure 1) both independently. In this way, the recirculation flows of the liquid phase (overflow) and the vapor phase (condensation) were also controlled. The stability of the aforementioned variables is reflected by an alarm (the PC detects the constancy of p and T within the interval

marked by the uncertainties of both quantities) which indicated the time when the phase samples should be removed to measure their densities. Equilibrium states were achieved in average time intervals of 15 min, and the compositions for the liquid x and vapor y phases were determined from the corresponding densities ρ_L and ρ_V of the mixtures. An independent regression was performed using a polynomial equation obtained previously, with known values of ($x \pm 0.0002$, $\rho \pm 0.02 \text{ kg}\cdot\text{m}^{-3}$) at a temperature of 298.15 K for mixtures synthetically prepared in the interval $\{x_1[0,1], \rho[\rho_2, \rho_1]\}$. So, the equation applied to the vapor-condensed phase of the alkyl propanoate (1) + alkane (2) has the form:

$$\rho_V = (\rho_1 - \rho_2)y_1 + \rho_2 + y_1y_2(a + by_1 + cy_1^2) \quad (1)$$

An Anton Paar, DMA-55, densimeter was used, and the temperature was controlled at ($T \pm 0.02$) K with a PolyScience 1166D circulating water bath, calibrated at each temperature with water and nonane. The correlation obtained with a least-squares procedure was excellent, with $r^2 > 0.99$, and the compositions of the liquid and vapor phases, calculated by eq 1, presented uncertainties of ± 0.002 . From values of the composition and density at each temperature, values were determined for the corresponding excess property of the systems studied, obtaining in this way the pairs ($x \pm 0.0002$, $v^E \pm 2 \cdot 10^{-9} \text{ m}^3 \cdot \text{mol}^{-1}$).

The refractive indices ($n_D \pm 0.0002$) shown in Table 1 were measured with an Abbe refractometer (Zuzi), model 320, whose working temperature (298.15 ± 0.02) K was achieved with the previously mentioned water bath.

3. MATHEMATICAL TREATMENT OF DATA

In this work, the mathematical treatment of experimental data was performed with a polynomial model established for Gibbs

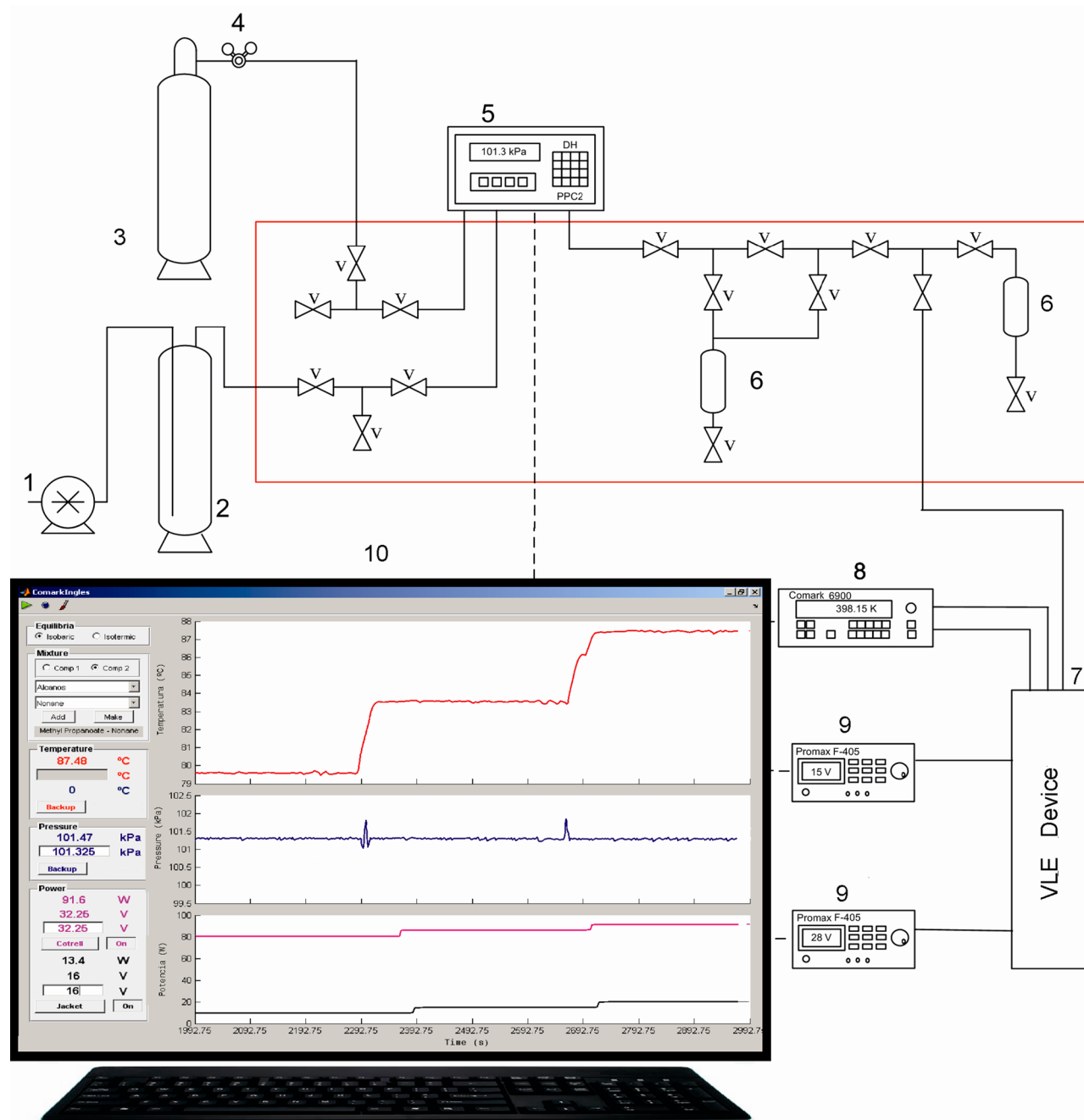


Figure 1. Scheme of auxiliary installation used for iso- p VLE measurements. 1, vacuum pump; 2, buffer tank; 3, N_2 ; 4, reduction valve; 5, pressure regulator PPC2; 6, buffer-tank; 7, VLE device; 8, digital thermometer; 9, power supply, V, valve; 10, PC-screen showing the variation of the experimental variables (p /kPa, T /K, w /watt) with time. The pressure peaks correspond to the addition/removal of the sample.

excess function, $g^E = g^E(p, T, x)$, whose general form was presented previously.²

$$g^E = z_1(1 - z_1)[g_0 + g_1z_1 + g_2z_1^2] \quad \text{with} \\ z_1(x, T) = \frac{x_1}{x_1 + k^{21}(T)x_2} \quad (2)$$

where k^{21} is a characteristic parameter of the model related to compounds 1 and 2. This parameter is identified differently depending of the property; so k_v^{21} for v^E , k_h^{21} for h^E , and k_g^{21} for g^E .

Both the active fraction z_1 , referred to the first compound of the binary, and the coefficients g_i are functions of the pressure p and the temperature T . In this way, the first and second

derivatives of eq 2 give rise to other quantities consistent with thermodynamic formalism:

$$h^E = g^E - T \left(\frac{\partial g^E}{\partial T} \right)_{p,x}, \quad c_p^E = -T \left(\frac{\partial^2 g^E}{\partial T^2} \right)_{p,x}, \quad s^E = - \left(\frac{\partial g^E}{\partial T} \right)_{p,x} \quad (3)$$

The following generic expression relates the coefficients g_i with p and T :

$$g_i(p, T) = g_{i1} + g_{i2}p^2 + g_{i3}pT + \frac{g_{i4}}{T} + g_{i5}T^2 \quad (4)$$

Table 3. Densities ρ and Excess Molar Volumes v^E for the Binaries Alkyl Propanoate (1) + Alkane (2) at Several Temperatures and Atmospheric Pressure^a

x_1	ρ kg·m ⁻³	$10^9 v^E$ m ³ ·mol ⁻¹	x_1	ρ kg·m ⁻³	$10^9 v^E$ m ³ ·mol ⁻¹	x_1	ρ kg·m ⁻³	$10^9 v^E$ m ³ ·mol ⁻¹
Methyl Propanoate (1) + Pentane (2)								
288.15 K								
0.0000	630.78	0	0.3382	714.27	517	0.6900	817.19	298
0.0597	644.23	207	0.3927	729.16	513	0.7581	839.01	221
0.0925	651.90	292	0.4420	743.09	480	0.8072	855.11	167
0.1507	665.97	388	0.4985	759.20	462	0.8487	868.74	144
0.2040	679.21	456	0.5461	773.25	417	0.8891	882.39	104
0.2614	693.95	494	0.5926	787.12	387	0.9538	904.73	42
0.3127	707.38	523	0.6407	801.96	326	1.0000	921.21	0
298.15 K								
0.0000	620.91	0	0.3389	703.72	543	0.6898	805.83	292
0.0641	635.16	238	0.3942	718.75	533	0.7559	826.88	217
0.0938	642.10	304	0.4459	733.12	516	0.8051	842.74	178
0.1482	654.98	420	0.4999	748.56	480	0.8499	857.54	135
0.2099	670.19	500	0.5478	762.56	438	0.8915	871.51	99
0.2574	682.36	515	0.5921	775.90	381	0.9601	894.98	44
0.3135	696.99	539	0.6434	791.33	355	1.0000	909.10	0
Methyl Propanoate (1) + Heptane (2)								
288.15 K								
0.0000	688.16	0	0.4021	754.13	904	0.7420	835.61	639
0.0584	696.10	243	0.4565	765.31	917	0.7927	850.46	549
0.1524	710.11	518	0.5036	775.51	909	0.8457	866.96	427
0.2121	719.49	692	0.5554	787.28	886	0.9530	903.48	158
0.2626	728.22	751	0.6032	798.81	838	1.0000	921.21	0
0.2841	731.88	801	0.6510	810.73	801			
0.3577	745.50	872	0.7008	824.05	720			
298.15 K								
0.0000	679.62	0	0.3827	740.59	947	0.7330	821.94	718
0.0606	687.94	214	0.4242	748.73	968	0.7758	834.28	616
0.1046	694.01	403	0.4831	760.98	965	0.8196	847.29	530
0.1706	703.97	588	0.5328	771.82	956	0.8646	861.68	393
0.2332	713.99	734	0.5887	784.89	895	0.9035	874.46	299
0.2863	722.89	849	0.6395	797.24	853	0.9591	893.83	142
0.3320	730.95	926	0.6831	808.46	794	1.0000	909.10	0
308.15 K								
0.0000	670.96	0	0.3462	723.99	973	0.7516	815.93	738
0.0460	676.88	221	0.3973	733.51	1020	0.7947	828.30	641
0.0974	683.97	414	0.4379	741.49	1033	0.8541	846.50	479
0.1499	691.60	583	0.5001	754.33	1035	0.8904	858.19	374
0.2093	700.71	745	0.5482	764.86	1014	0.9494	878.31	193
0.2472	706.83	825	0.6013	777.11	973	1.0000	896.91	0
0.2655	709.84	864	0.6438	787.52	912			
0.3021	716.16	913	0.7002	801.92	835			
318.15 K								
0.0000	662.33	0	0.3492	714.64	1069	0.7022	791.53	880
0.0540	669.26	247	0.3962	723.32	1104	0.7463	803.36	787
0.1006	675.53	443	0.4482	733.48	1104	0.7960	817.45	667
0.1635	684.64	636	0.5006	744.15	1108	0.8421	831.26	538
0.1984	689.88	739	0.5540	755.69	1085	0.8911	846.73	394
0.2627	699.98	905	0.5928	764.54	1044	0.9487	866.17	197
0.2892	704.22	984	0.6531	779.07	955	1.0000	884.71	0
328.15 K								
0.0000	653.61	0	0.3858	711.54	1135	0.7484	792.52	842
0.0434	659.02	216	0.4619	725.95	1181	0.7954	805.67	717
0.1000	666.42	466	0.5057	734.85	1172	0.8441	820.03	577
0.1539	673.86	678	0.5548	745.30	1147	0.8954	836.18	397
0.2137	682.78	840	0.6006	755.62	1098	0.9351	849.33	255
0.2630	690.45	966	0.6513	767.59	1029	1.0000	872.22	0

Table 3. continued

x_1	ρ kg·m ⁻³	$10^9 v^E$ m ³ ·mol ⁻¹	x_1	ρ kg·m ⁻³	$10^9 v^E$ m ³ ·mol ⁻¹	x_1	ρ kg·m ⁻³	$10^9 v^E$ m ³ ·mol ⁻¹
328.15 K								
0.3610	707.07	1109	0.7013	780.04	948			
Methyl Propanoate (1) + Nonane (2)								
288.15 K								
0.0000	721.65	0	0.3526	761.75	1002	0.6930	824.65	947
0.0638	727.45	298	0.4001	768.71	1062	0.7454	837.57	858
0.0962	730.67	417	0.4322	773.78	1078	0.7911	849.84	754
0.1483	736.11	592	0.4985	784.90	1098	0.8391	863.79	629
0.2104	743.23	745	0.5504	794.42	1081	0.8911	880.25	478
0.2364	746.30	818	0.5954	803.25	1058	0.9477	900.31	260
0.2979	754.20	924	0.6449	813.66	1016	1.0000	921.21	0
298.15 K								
0.0000	713.85	0	0.3489	752.48	1032	0.7510	828.64	868
0.0519	718.48	236	0.4090	761.11	1114	0.7937	839.79	790
0.1041	723.58	424	0.4474	767.10	1135	0.8444	854.36	646
0.1448	727.66	584	0.5033	776.37	1152	0.9002	871.96	464
0.1889	732.52	699	0.6015	794.61	1123	0.9516	890.02	255
0.2498	739.65	844	0.6609	807.17	1046	1.0000	909.10	0
0.2949	745.26	944	0.7048	817.21	974			
308.15 K								
0.0000	705.96	0	0.3585	744.82	1110	0.6990	805.43	1045
0.0618	711.31	300	0.4102	752.25	1157	0.7476	817.03	947
0.1007	715.02	448	0.4567	759.29	1198	0.7960	829.48	836
0.1650	721.49	677	0.4962	765.69	1215	0.8477	844.14	675
0.1941	724.61	766	0.5559	776.15	1199	0.8947	858.80	495
0.2601	732.22	927	0.5986	784.17	1182	0.9504	877.94	252
0.2902	735.94	982	0.6514	794.91	1126	1.0000	896.91	0
318.15 K								
0.0000	698.06	0	0.3621	736.39	1162	0.6972	794.52	1126
0.0587	703.05	283	0.3940	740.75	1210	0.7464	805.96	1025
0.1139	708.17	503	0.4491	748.79	1263	0.7904	816.99	919
0.1410	710.78	612	0.4889	755.06	1273	0.8414	831.04	747
0.2148	718.51	841	0.5458	764.61	1275	0.8899	845.62	566
0.2624	723.90	967	0.6011	774.72	1246	0.9498	865.72	290
0.3145	730.23	1077	0.6538	785.15	1201	1.0000	884.71	0
328.15 K								
0.0000	690.17	0	0.3128	721.06	1155	0.7484	795.44	1110
0.0562	694.80	280	0.3582	726.72	1245	0.7963	807.38	965
0.0989	698.61	460	0.4509	739.58	1351	0.8469	821.01	803
0.1503	703.45	663	0.5045	747.90	1364	0.9004	836.96	585
0.1813	706.43	796	0.5545	756.22	1362	0.9501	853.63	315
0.1940	707.71	844	0.6005	764.42	1342	1.0000	872.22	0
0.2651	715.48	1036	0.6523	774.55	1271			
Ethyl Propanoate (1) + Pentane (2)								
288.15 K								
0.0000	630.78	0	0.3525	722.09	291	0.6974	814.34	127
0.0503	643.39	118	0.3947	733.28	283	0.7488	828.17	99
0.1017	656.50	195	0.4496	747.92	259	0.7974	841.13	85
0.1511	669.25	246	0.5009	761.70	225	0.8477	854.65	59
0.2025	682.62	274	0.5519	775.33	203	0.8951	867.40	38
0.2551	696.41	289	0.5987	787.90	173	0.9482	881.60	23
0.3012	708.53	294	0.6449	800.24	156	1.0000	895.58	0
298.15 K								
0.0000	620.90	0	0.3594	713.37	289	0.7061	805.64	119
0.0545	634.55	113	0.4062	725.70	280	0.7498	817.26	104
0.1013	646.47	173	0.4575	739.37	249	0.8007	830.93	70
0.1538	659.85	234	0.5083	752.81	232	0.8535	844.98	57
0.2051	673.10	265	0.5600	766.57	206	0.9054	858.85	36
0.2540	685.81	283	0.6060	778.84	182	0.9511	871.06	19

Table 3. continued

x_1	ρ kg·m ⁻³	$10^9 \nu^E$ m ³ ·mol ⁻¹	x_1	ρ kg·m ⁻³	$10^9 \nu^E$ m ³ ·mol ⁻¹	x_1	ρ kg·m ⁻³	$10^9 \nu^E$ m ³ ·mol ⁻¹
298.15 K								
0.3038	698.80	291	0.6559	792.17	152	1.0000	884.15	0
Ethyl Propanoate (1) + Heptane (2)								
288.15 K								
0.0000	688.16	0	0.3473	745.24	709	0.7532	830.95	504
0.0524	695.91	179	0.4004	755.32	717	0.7965	841.54	433
0.0988	703.07	303	0.4483	764.49	745	0.8566	856.59	342
0.1463	710.63	412	0.5023	775.33	737	0.9037	868.82	258
0.1941	718.60	482	0.5493	785.04	721	0.9502	881.54	135
0.2514	728.31	577	0.6523	807.55	624	1.0000	895.58	0
0.3018	737.02	666	0.7155	821.91	573			
298.15 K								
0.0000	679.62	0	0.4010	745.76	764	0.7456	818.46	548
0.0502	687.02	154	0.4502	755.12	780	0.7933	829.93	466
0.0966	693.85	330	0.5047	765.87	780	0.8547	845.07	371
0.1618	704.16	469	0.5980	785.24	727	0.9029	857.64	253
0.2400	717.15	593	0.6478	796.11	678	0.9520	870.77	136
0.3102	729.24	692	0.6968	807.10	624	1.0000	884.15	0
308.15 K								
0.0000	670.96	0	0.3520	727.08	778	0.6957	796.27	656
0.0489	677.99	172	0.4029	736.28	821	0.7472	808.10	576
0.0972	685.13	326	0.4400	743.31	818	0.8001	820.72	473
0.1622	695.08	508	0.5033	755.53	825	0.8549	834.09	383
0.2109	702.86	614	0.5515	765.29	798	0.8932	843.97	280
0.2409	707.93	639	0.6049	776.34	771	0.9490	858.62	147
0.3084	719.36	741	0.6546	787.12	709	1.0000	872.62	0
318.15 K								
0.0000	662.33	0	0.3494	717.01	820	0.7022	787.15	680
0.0535	669.87	199	0.4057	727.08	861	0.7467	797.21	612
0.0979	676.31	351	0.4487	735.05	873	0.7935	808.20	519
0.1459	683.47	500	0.5052	745.90	865	0.8452	820.60	428
0.2045	692.71	618	0.5520	755.16	850	0.8929	832.60	311
0.2620	702.04	725	0.5969	764.38	815	0.9484	847.05	162
0.3009	708.59	775	0.6529	776.27	752	1.0000	861.08	0
328.15 K								
0.0000	653.61	0	0.3519	707.73	873	0.7023	776.34	732
0.0528	660.86	219	0.4084	717.71	911	0.7443	785.77	655
0.1065	668.58	398	0.4478	724.83	935	0.7989	798.40	548
0.1619	676.84	553	0.5074	736.13	922	0.8593	812.97	403
0.2123	684.53	692	0.5522	744.86	909	0.8983	822.61	318
0.2511	690.83	747	0.6033	755.17	872	0.9494	835.87	158
0.3081	700.22	832	0.6454	764.10	801	1.0000	849.41	0
Ethyl Propanoate (1) + Nonane (2)								
288.15 K								
0.0000	721.65	0	0.3579	763.17	873	0.6935	819.81	789
0.0545	727.07	189	0.4121	770.89	926	0.7463	830.79	715
0.1159	733.36	414	0.4620	778.51	939	0.7907	840.69	621
0.1434	736.52	458	0.5039	785.25	932	0.8950	866.09	362
0.2218	745.49	669	0.5537	793.58	927	0.9488	880.62	195
0.2412	747.88	703	0.6035	802.47	888	1.0000	895.58	0
0.3158	757.46	818	0.6328	807.91	864			
298.15 K								
0.0000	713.85	0	0.4078	761.40	950	0.7410	819.48	756
0.0538	718.94	223	0.4592	769.02	971	0.7883	829.57	685
0.0883	722.45	332	0.4988	775.19	974	0.8559	845.47	494
0.1420	728.05	511	0.5511	783.72	967	0.9034	857.27	367
0.2152	736.31	689	0.5917	790.84	924	0.9521	870.29	205
0.3007	746.83	837	0.6562	802.56	878	1.0000	884.15	0
0.3555	754.11	899	0.6962	810.32	828			

Table 4. Coefficients v_{ij} and Standard Deviations s , Obtained in the Correlation of $v^E = \varphi(x, T)$ by eq 2 and eq 19 for Coefficients v_{ij} of the Binaries Alkyl Propanoate + Alkane

	methyl propanoate			ethyl propanoate		
	pentane	heptane	nonane	pentane	heptane	nonane
v_{00}	$-2.638 \cdot 10^6$	$6.021 \cdot 10^6$	$2.628 \cdot 10^7$	$3.514 \cdot 10^3$	$1.389 \cdot 10^6$	$-1.680 \cdot 10^7$
v_{01}	$1.346 \cdot 10^4$	$-4.370 \cdot 10^4$	$-1.721 \cdot 10^5$	$1.288 \cdot 10^3$	$-1.299 \cdot 10^4$	$1.120 \cdot 10^5$
v_{02}		$1.010 \cdot 10^2$	$3.089 \cdot 10^2$		$4.337 \cdot 10^1$	$-1.657 \cdot 10^2$
v_{10}	$5.705 \cdot 10^6$	$-1.371 \cdot 10^7$	$-8.479 \cdot 10^7$	$-1.615 \cdot 10^6$	$5.469 \cdot 10^6$	$7.666 \cdot 10^7$
v_{11}	$-2.698 \cdot 10^4$	$8.882 \cdot 10^4$	$5.408 \cdot 10^5$	$1.306 \cdot 10^3$	$-3.243 \cdot 10^4$	$-5.132 \cdot 10^5$
v_{12}		$-1.701 \cdot 10^2$	$-8.968 \cdot 10^2$		$3.340 \cdot 10^1$	$8.351 \cdot 10^2$
v_{20}	$-2.970 \cdot 10^6$	$8.362 \cdot 10^6$	$8.693 \cdot 10^7$	$1.250 \cdot 10^6$	$-4.421 \cdot 10^6$	$-8.237 \cdot 10^7$
v_{21}	$1.412 \cdot 10^4$	$-5.184 \cdot 10^4$	$-5.562 \cdot 10^5$	$-2.110 \cdot 10^3$	$2.840 \cdot 10^4$	$5.476 \cdot 10^5$
v_{22}		$9.241 \cdot 10^1$	$9.083 \cdot 10^2$		$-3.937 \cdot 10^1$	$-8.969 \cdot 10^2$
k_v^{21}	1.197	1.520	1.849	1.004	1.276	1.552
$s(v^E)$ ($T = 288.15$ K)	9	10	16	4	12	8
$s(v^E)$ ($T = 298.15$ K)	11	14	11	4	11	11
$s(v^E)$ ($T = 308.15$ K)		10	17		8	10
$s(v^E)$ ($T = 318.15$ K)		11	11		6	15
$s(v^E)$ ($T = 328.15$ K)		10	10		8	7

$$\frac{dz(k, T)}{dT} = \frac{\partial z}{\partial k} \left(\frac{dk}{dT} \right) = \frac{x(1-x)}{[x + k(1-x)]^2} \left(\frac{dk}{dT} \right) \quad (9)$$

The variation of the k -parameter with T for the binaries elected must be analyzed first, as it could be negligible. The systems considered generate gradients less than 0.5 %; so eqs 5 to 7 can be conveniently simplified.

Another important property to take into account in the treatment of VLE data are the activity coefficients obtained by:

$$RT \ln \gamma_i = \bar{g}_i^E = g^E - \sum_{k \neq i} x_k \left(\frac{\partial g^E}{\partial x_k} \right)_{p, T, x_j \neq k, i} \quad (10)$$

Which, with eq 2 give the following expression,

$$RT \ln \gamma_i = z(1-z) \sum_{j=0}^2 g_j z^j + (1-x_i) \cdot \left[\sum_{j=0}^3 (j+1)(g_j - g_{j-1}) z^j \right] k \left(\frac{z}{x_i} \right)^2 \quad (11)$$

a generic form that is fulfilled when $g_{-1} = g_3 = 0$. From this latter equation, the activity coefficients at infinite dilution, γ_i^∞ , are determined with the particular expressions,

$$\ln \gamma_1^\infty = \lim_{x_1 \rightarrow 0} \ln \gamma_1 \equiv \lim_{z_1 \rightarrow 0} \ln \gamma_1 = \frac{g_0}{kRT_{b,2}^0} \quad (12)$$

$$\ln \gamma_2^\infty = \lim_{x_2 \rightarrow 0} \ln \gamma_2 \equiv \lim_{z_2 \rightarrow 0} \ln \gamma_2 = \frac{k(g_0 + g_1 + g_2)}{RT_{b,1}^0} \quad (13)$$

Data were also treated by applying the original version of the NRTL model,¹⁶ which presents the following generic form.

$$g^E = RT x_1 x_2 \sum_{i=1}^2 \sum_{j=1}^2 \frac{G_{ij} \tau_{ij}}{x_i G_{ij} + x_j} \quad \forall i \neq j \quad (14)$$

But with a different parametrization, in accordance with the extended form proposed by Ko et al.,²¹ for the τ_{ij} .

$$\tau_{ij} = \Delta g_{ij0} + \frac{\Delta g_{ij1}}{T} + \Delta g_{ij2} \ln T \quad (15)$$

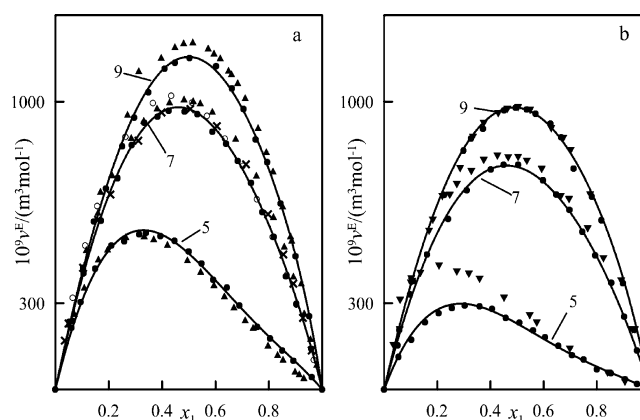


Figure 3. Representation of experimental v^E values (●), and correlation curves (—) using eqs 2 and 19, for the binary systems: a, x_1 methyl propanoate + x_2 C_nH_{2n+2} ; b, x_1 ethyl propanoate + x_2 C_nH_{2n+2} , and comparison with those from literature ×, ref 14; ▲, ref 11; ▼, ref 12; ○, ref 10. Labels indicate n .

this extension was necessary to achieve a better fit, especially of the enthalpies at different temperatures. For this model, the expression for the enthalpy is:

$$\frac{h^E}{RT^2} = -x_1 x_2 \left\{ \tau'_{12} e^{-\alpha_{12} \tau'_{12}} \left[\frac{x_1 e^{-\alpha_{12} \tau'_{12}} + x_2 (1 + \tau_{12})}{(x_1 e^{-\alpha_{12} \tau'_{12}} + x_2)^2} \right] + \tau'_{21} e^{-\alpha_{21} \tau'_{21}} \left[\frac{x_2 e^{-\alpha_{21} \tau'_{21}} + x_1 (1 + \tau_{21})}{(x_2 e^{-\alpha_{21} \tau'_{21}} + x_1)^2} \right] \right\} \quad (16)$$

where $\tau'_{ij} = (d\tau_{ij}/dT)$.

Note the complexity of eq 16. Logically, the corresponding second derivative to obtain τ_p^E produces an even longer expression, which because of its extension we decided not to include here. A mathematical tool was used to treat the data that permitted analytical deductions to be made. The generic mathematical expression for the activity coefficients is as follows:

$$\ln \gamma_i = x_j^2 \left[\tau_{ij} \left(\frac{\exp(-\alpha_{ij} \tau_{ij})}{x_i + x_j \exp(-\alpha_{ij} \tau_{ij})} \right)^2 + \frac{\tau_{ij} \exp(-\alpha_{ij} \tau_{ij})}{x_j + x_i \exp(-\alpha_{ij} \tau_{ij})} \right] \quad (17)$$

Table 5. Experimental Vapor Pressures of Pure Compounds^a

T/K	p_i^o /kPa	T/K	p_i^o /kPa	T/K	p_i^o /kPa	T/K	p_i^o /kPa	T/K	p_i^o /kPa	T/K	p_i^o /kPa
Methyl Propanoate						Ethyl Propanoate					
335.15	55.00	353.81	105.00	374.90	200.00	359.57	67.50	380.40	130.00	401.00	230.00
336.38	57.50	355.23	110.00	375.77	205.00	360.66	70.00	381.67	135.00	401.83	235.00
337.53	60.00	356.53	115.00	376.63	210.00	361.72	72.50	382.91	140.00	402.65	240.00
338.61	62.50	357.87	120.00	377.52	215.00	362.74	75.00	384.15	145.00	403.46	245.00
339.76	65.00	359.16	125.00	378.30	220.00	363.71	77.50	385.32	150.00	404.25	250.00
340.79	67.50	360.42	130.00	379.14	225.00	364.69	80.00	386.47	155.00	405.04	255.00
341.81	70.00	361.65	135.00	379.96	230.00	365.63	82.50	387.60	160.00	405.79	260.00
342.79	72.50	362.80	140.00	380.72	235.00	366.55	85.00	388.69	165.00	406.56	265.00
343.75	75.00	363.97	145.00	381.51	240.00	367.47	87.50	389.77	170.00	407.30	270.00
344.68	77.50	365.05	150.00	382.25	245.00	368.35	90.00	390.81	175.00	408.03	275.00
345.59	80.00	366.15	155.00	383.03	250.00	369.21	92.50	391.83	180.00	408.75	280.00
346.49	82.50	367.22	160.00	383.74	255.00	Pentane					
347.35	85.00	368.27	165.00	384.47	260.00	298.91	70.00	314.26	120.00	331.51	205.00
348.20	87.50	369.26	170.00	385.21	265.00	299.82	72.50	315.50	125.00	332.34	210.00
349.03	90.00	370.25	175.00	385.87	270.00	300.77	75.00	316.70	130.00	333.15	215.00
349.83	92.50	371.22	180.00	386.61	275.00	301.65	77.50	317.87	135.00	333.95	220.00
350.62	95.00	372.20	185.00	387.28	280.00	302.52	80.00	319.01	140.00	334.73	225.00
352.34	100.00	373.12	190.00			303.38	82.50	320.11	145.00	335.50	230.00
352.72	101.32	374.01	195.00			304.22	85.00	321.17	150.00	336.28	235.00
Ethyl Propanoate						305.02	87.50	322.24	155.00	337.02	240.00
348.07	45.00	370.06	95.00	392.85	185.00	305.81	90.00	323.25	160.00	337.75	245.00
349.55	47.50	370.87	97.50	393.81	190.00	306.62	92.50	324.26	165.00	338.47	250.00
350.96	50.00	371.73	100.00	394.77	195.00	307.37	95.00	325.24	170.00	339.19	255.00
352.34	52.50	372.18	101.32	395.72	200.00	308.12	97.50	326.18	175.00	339.89	260.00
353.66	55.00	373.31	105.00	396.64	205.00	308.87	100.00	327.12	180.00	340.59	265.00
354.91	57.50	374.84	110.00	397.55	210.00	309.23	101.32	328.03	185.00	341.27	270.00
356.15	60.00	376.29	115.00	398.43	215.00	310.28	105.00	328.93	190.00	341.94	275.00
357.32	62.50	377.70	120.00	399.31	220.00	311.64	110.00	329.80	195.00	342.60	280.00
358.48	65.00	379.08	125.00	400.17	225.00	312.97	115.00	330.66	200.00		

^aUncertainties u are: $u(T) = \pm 0.01$ K and $u(p) = \pm 0.02$ kPa.

Table 6. Coefficients of the Antoine Equation: $\log(p_i^o/\text{kPa}) = A - B/[(T/\text{K}) - C]$ and Acentric Factors ω for Pure Compounds Used in This Work and Comparison with Those Found in Literature

compound	A	B	C	ω^a	range T/K	reference
methyl propanoate	6.12238	1187.36	64.20	0.345	335 to 387	this work
	(2.51985)	(2.2378)	(0.121)			
	6.49972	1398.49	41.22	0.347 ^b	315 to 346	22
ethyl propanoate	6.60420	1478.55	30.07	0.378	330 to 364	23
	6.15949	1279.38	64.14	0.390	348 to 409	this work
	(2.63289)	(2.3432)	(0.117)			
pentane	6.33431	1404.22	47.58	0.390 ^b	315 to 388	24
	6.1440	1274.70	64.16	0.391	276 to 396	25
	5.91964	1027.53	46.70	0.251	299 to 342	this work
	(2.39332)	(2.1886)	(0.100)			
heptane	6.02546	1086.22	38.76	0.260	309 to 323	4
	6.01075	1251.31	59.06	0.349	346 to 410	1
	6.09705	1451.26	68.93	0.442	396 to 467	1
nonane				0.249 ^b		

^aValues obtained from eq 21. ^bValues estimated by Lee–Kesler.²⁷

From which it can be deduced that γ_i^∞ , taking into account the conditions of eqs 12 and 13, is given by the expression:

$$\ln \gamma_i^\infty = \lim_{x_i \rightarrow 0} \ln \gamma_i = \tau_{ji} + \tau_{ij} \exp(-\alpha \tau_{ij}) \quad i, j = 1, 2 \quad (18)$$

4. EXPERIMENTAL RESULTS AND DISCUSSION

4.1. Excess Properties. For the binaries selected, represented generically by $\text{CH}_3\text{CH}_2\text{CO}_2\text{C}_n\text{H}_{2u+1}$ ($u = 1, 2$) + $\text{C}_n\text{H}_{2n+2}$ ($n = 5, 7, 9$), the v^E were determined at every 10 K in the interval (288.15 to 328.15) K, obtained from the direct values of the pairs (x, ρ) , except for the systems with pentane due to their

low boiling point ($T_b^o = 309.21 \text{ K}^{17}$). The values calculated are recorded in Table 3 and in Figure 2a,b. The coordinates ($x, T/K, p v^E/\text{J}\cdot\text{mol}^{-1}$) with the corresponding fitting curves, together with the surfaces generated by $h^E = h^E(x, T)$ (see refs 6–8) are represented graphically in three dimensions for the same systems. In all cases, the excess property was correlated by an equation similar to that of eq 2, but using a simpler expression than eq 4 for the coefficients v_i , if we refer to volumes,

$$v_i(T) = v_{i1} + v_{i2}T + \frac{v_{i3}}{T} \quad (19)$$

The coefficients were obtained using a linear correlation procedure with an algorithm implemented in MATLAB minimizing the standard deviation of the v_i^E , which for any generic property, y^E , is

$$s(y^E) = \left[\sum_1^N (y_{i,\text{exp}}^E - y_{i,\text{cal}}^E)^2 / (N - 1) \right]^{1/2} \quad (20)$$

where N is the number of experimental points for the property considered.

Values of the parameter $k_v^{21}(T)$ for the volumetric fraction, eq 2, were calculated for each mixture as indicated previously^{4,5} and show a negligible variation with temperature. Coefficients of eq 19 obtained for each of the systems are recorded in Table 4, which also shows the results of $s(v^E)$ for each system at each temperature. The parameters of goodness of fit in Table 4 and the representations in Figure 2 show that the quality of fit is good, with a mean global error for the set lower than 2%. Figure 3a,b shows a comparison between the curve in this work and those published in the literature. On the whole, the current data show a good agreement with all the data in the literature, except for those determined by our research team in 1997 (ref 12), which show inexplicable average differences, especially high, close to 50% around the zone of $x < 0.6$ for the binary ethyl propanoate + pentane.

In the vertical plane shown in Figure 2a,b, a positive value can be observed for the slope $p(\partial v^E/\partial T)_x > 0$, although the increase in temperature has very little influence on the volumetric expansions and, in general, on the excess properties. On the one hand, the increase in thermal agitation only produces a slight increase in Brownian motion that barely weakens the intermolecular attractions at all; the variation in expansive and endothermic effects (see refs 6 to 8 and surfaces $h^E = h^E(x, T)$ in Figure 2) with the number of groups $-\text{CH}_2-$ of the compounds is as expected. On the other hand, the increase in hydrocarbon chain length for a fixed ester increases the surfaces in contact, positively increasing the values of the mixing properties. However, the increase in alkanolic chain length in the propanoates, which present a slight increase in dipolar moment, have a negative effect on the mixing properties since the irruption of the hydrocarbon makes the dipole–dipole effect diminish and also the endothermic and expansive effects of the mixtures.

4.2. Vapor Pressures. The values (T, p_i^o) that make up the vapor–liquid saturation curve are important because of their influence on the calculations of phase equilibria in solutions. Hence, for this work measurements have been made for three of the substances used, methyl and ethyl propanoate and pentane, over a range of pressures from (45 to 280) kPa, since the values for heptanes and nonane have been presented recently.¹ Values were measured in the same installation as those shown in Figure 1, and the results are recorded in Table 5. For each compound, a correlation was carried out using Antoine's equation,

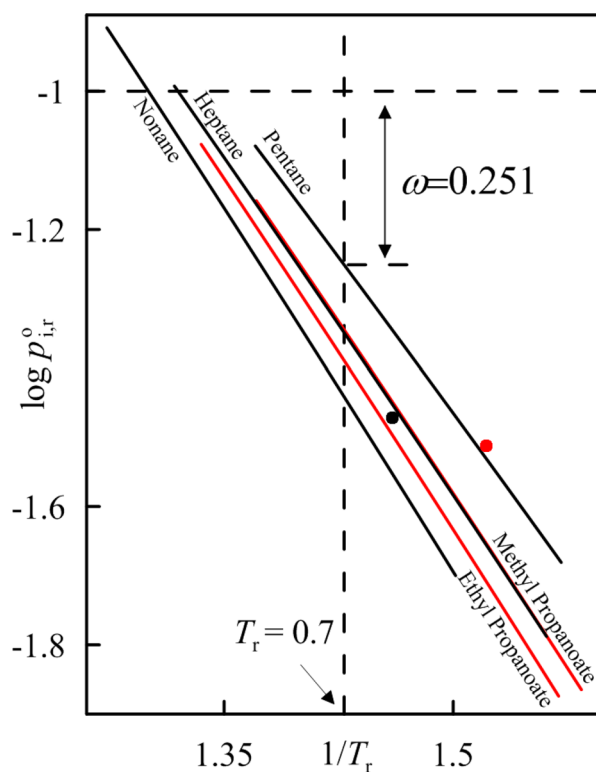


Figure 4. Vapor pressure lines in reduced coordinates for alkyl (methyl, ethyl) propanoate and alkanes (pentane, heptane, nonane) and position of the azeotropic points for: red ●, methyl propanoate + heptane; black ●, ethyl propanoate + heptane.

applying a nonlinear regression procedure implemented in Matlab. The parameters obtained are shown in Table 6, where they are compared with those from the literature. The reduced form of Antoine's equation adopts a similar mathematical expression, where the new parameters a , b , and c are related to the original ones A , B , and C through simple expressions such as the one shown in a previous work,²⁶ considering as boundary conditions those of the critical point.

$$\log p_{i,r}^o = a - \frac{b}{T_r - c} \quad (21)$$

However, since the validity of Antoine's equation is limited to the range of working pressures and which in our case does not reach the critical point, it is appropriate to recalculate values of a , b , and c for the range of measurements, correlating the experimental data of Table 5, but as reduced quantities, using the same procedure shown before for Antoine's equation. In this way, the acentric factor of each pure compound is calculated from the expression: $(0.7 - c)(\omega + a + 1) = b$, which are shown in Table 6; the comparison with other values recorded in the literature and with those estimated by Lee–Kesler²⁷ is good. Values of ω obtained are used to calculate the parameters of iso- p VLE. Figure 4 shows representations of the vapor pressures lines in reduced coordinates for the products used here.

4.3. Presentation of iso- p VLE Data. The experimental values of binaries $\text{H}_5\text{C}_2\text{CO}_2\text{C}_u\text{H}_{2u+1}$ ($u = 1, 2$) (1) + $\text{C}_n\text{H}_{2n+2}$ ($n = 5, 7, 9$) (2) that characterize the iso-101.32 kPa VLE (p, T, x, y) are recorded in Table 7. With these values, the representations T vs x_1, y_1 and $(y_1 - x_1)$ vs x_1 of Figure 5a–f have been made. The graphs show the presence of azeotropes in the binaries with heptane and a comparison of the data obtained with those of a previous work for methyl propanoate + heptane in Figure 5b,

Table 7. Experimental Values and Calculated Quantities for the iso-101.32 kPa VLE of the Binaries Alkyl Propanoate + Alkane^a

T/K	x_1	y_1	γ_1	γ_2	g^E/RT	T/K	x_1	y_1	γ_1	γ_2	g^E/RT
Methyl Propanoate (1) + Pentane (2)											
309.23	0.000	0.000		1.000	0.000	319.91	0.607	0.218	1.157	1.428	0.229
309.45	0.023	0.012	2.735	1.004	0.027	320.46	0.633	0.228	1.136	1.483	0.226
309.56	0.030	0.016	2.766	1.003	0.033	322.85	0.690	0.263	1.092	1.565	0.199
309.78	0.048	0.026	2.655	1.006	0.052	324.81	0.731	0.297	1.078	1.624	0.185
310.11	0.074	0.037	2.459	1.011	0.076	328.54	0.792	0.362	1.051	1.717	0.151
310.60	0.109	0.052	2.279	1.018	0.105	330.73	0.823	0.401	1.032	1.783	0.128
311.09	0.153	0.065	2.007	1.039	0.139	336.98	0.897	0.539	1.013	1.988	0.083
311.65	0.187	0.079	1.935	1.048	0.162	339.82	0.921	0.609	1.009	2.055	0.065
312.30	0.230	0.093	1.791	1.068	0.185	341.77	0.936	0.662	1.009	2.098	0.055
312.83	0.268	0.105	1.699	1.089	0.205	343.64	0.948	0.710	1.003	2.106	0.042
313.48	0.308	0.117	1.602	1.115	0.220	346.76	0.968	0.805	1.003	2.155	0.027
313.88	0.330	0.124	1.564	1.127	0.227	348.47	0.979	0.862	1.006	2.182	0.022
314.47	0.373	0.134	1.464	1.167	0.239	349.75	0.986	0.903	1.004	2.185	0.015
315.00	0.404	0.144	1.416	1.195	0.247	350.56	0.990	0.930	1.003	2.231	0.011
315.58	0.436	0.153	1.358	1.227	0.249	351.35	0.994	0.959	1.004	2.283	0.008
316.27	0.469	0.164	1.309	1.261	0.250	352.01	0.997	0.979	1.001	2.239	0.004
317.04	0.504	0.176	1.269	1.300	0.250	352.75	1.000	1.000	1.000		0.000
317.95	0.546	0.191	1.225	1.354	0.248						
Methyl Propanoate (1) + Heptane (2)											
371.38	0.000	0.000		1.000	0.000	352.55	0.593	0.695	1.176	1.324	0.211
369.65	0.018	0.053	1.826	1.017	0.027	352.43	0.612	0.705	1.159	1.351	0.207
368.32	0.032	0.094	1.850	1.025	0.044	352.32	0.635	0.717	1.140	1.383	0.202
366.14	0.057	0.162	1.896	1.037	0.071	352.29	0.688	0.745	1.096	1.456	0.180
362.51	0.119	0.291	1.817	1.045	0.110	352.22	0.711	0.758	1.080	1.499	0.172
360.13	0.163	0.365	1.791	1.057	0.141	352.08	0.738	0.775	1.069	1.542	0.163
359.19	0.189	0.401	1.741	1.059	0.151	351.98	0.766	0.791	1.054	1.609	0.152
358.60	0.208	0.424	1.704	1.061	0.158	351.92	0.795	0.810	1.043	1.671	0.139
356.95	0.270	0.483	1.567	1.089	0.184	351.88	0.824	0.830	1.031	1.748	0.124
355.90	0.320	0.525	1.487	1.109	0.197	351.86	0.851	0.851	1.024	1.820	0.109
355.53	0.338	0.542	1.470	1.111	0.200	351.91	0.880	0.873	1.014	1.922	0.091
355.00	0.363	0.561	1.441	1.124	0.207	351.95	0.902	0.891	1.009	2.006	0.077
354.75	0.382	0.573	1.405	1.139	0.211	352.05	0.924	0.910	1.004	2.109	0.061
354.45	0.401	0.585	1.380	1.152	0.214	352.14	0.940	0.929	1.003	2.157	0.048
354.28	0.416	0.595	1.359	1.161	0.215	352.26	0.956	0.944	0.999	2.257	0.035
354.02	0.439	0.609	1.329	1.176	0.216	352.38	0.970	0.961	0.999	2.278	0.024
353.83	0.454	0.618	1.311	1.188	0.217	352.53	0.981	0.975	0.996	2.391	0.013
353.50	0.485	0.635	1.276	1.214	0.218	352.60	0.987	0.983	0.996	2.450	0.007
353.20	0.515	0.651	1.243	1.246	0.219	352.65	0.992	0.989	0.996	2.520	0.003
352.94	0.541	0.667	1.222	1.267	0.217	352.75	1.000	1.000	1.000		0.000
352.74	0.568	0.680	1.193	1.303	0.215						
Methyl Propanoate (1) + Nonane (2)											
423.90	0.000	0.000		1.000	0.000	361.07	0.636	0.924	1.125	1.458	0.212
420.88	0.010	0.076	1.402	1.001	0.004	360.03	0.674	0.932	1.104	1.511	0.201
418.00	0.020	0.149	1.453	1.002	0.009	358.96	0.716	0.939	1.081	1.621	0.193
412.86	0.040	0.271	1.467	1.004	0.019	358.14	0.749	0.946	1.067	1.670	0.178
408.40	0.059	0.366	1.492	1.006	0.029	357.41	0.780	0.952	1.052	1.770	0.165
403.88	0.079	0.453	1.502	1.007	0.039	356.75	0.804	0.957	1.047	1.827	0.155
400.83	0.094	0.506	1.504	1.009	0.047	356.34	0.818	0.960	1.046	1.846	0.148
398.08	0.110	0.552	1.499	1.010	0.053	356.12	0.834	0.963	1.036	1.899	0.136
394.50	0.133	0.608	1.478	1.012	0.062	355.89	0.844	0.965	1.034	1.911	0.129
392.60	0.147	0.634	1.461	1.016	0.069	355.53	0.864	0.968	1.024	2.023	0.116
387.71	0.183	0.699	1.447	1.018	0.083	355.40	0.869	0.969	1.023	2.057	0.114
384.71	0.211	0.735	1.425	1.020	0.091	354.85	0.896	0.975	1.015	2.157	0.094
382.29	0.242	0.762	1.369	1.033	0.101	354.39	0.920	0.980	1.008	2.284	0.073
379.14	0.280	0.794	1.332	1.047	0.114	354.13	0.933	0.983	1.004	2.396	0.062
376.09	0.316	0.818	1.320	1.077	0.138	353.89	0.946	0.986	1.001	2.481	0.050
372.60	0.370	0.846	1.277	1.122	0.163	353.69	0.956	0.988	0.999	2.605	0.041
370.15	0.410	0.863	1.256	1.166	0.184	353.53	0.966	0.990	0.997	2.696	0.031
368.03	0.454	0.877	1.226	1.213	0.198	353.37	0.974	0.992	0.995	2.850	0.023
366.24	0.492	0.890	1.204	1.253	0.206	353.17	0.982	0.995	0.995	2.884	0.014

Table 7. continued

T/K	x_1	y_1	γ_1	γ_2	g^E/RT	T/K	x_1	y_1	γ_1	γ_2	g^E/RT
Methyl Propanoate (1) + Nonane (2)											
364.62	0.533	0.902	1.181	1.290	0.208	352.99	0.989	0.996	0.996	3.069	0.009
363.30	0.568	0.910	1.161	1.337	0.210	352.79	0.993	0.998	0.999	3.057	0.007
361.90	0.610	0.919	1.138	1.402	0.211	352.75	1.000	1.000	1.000		0.000
Ethyl Propanoate (1) + Pentane (2)											
309.23	0	0		1	0	323.15	0.531	0.109	1.184	1.236	0.189
309.67	0.016	0.003	2.146	0.999	0.011	323.87	0.548	0.115	1.168	1.249	0.186
309.99	0.032	0.006	2.059	1.002	0.025	324.73	0.568	0.122	1.152	1.265	0.182
310.30	0.044	0.009	2.112	1.002	0.035	325.59	0.590	0.129	1.134	1.289	0.178
310.56	0.057	0.011	2.061	1.004	0.044	327.89	0.637	0.149	1.101	1.333	0.165
310.88	0.073	0.014	1.974	1.008	0.057	329.08	0.661	0.160	1.085	1.364	0.159
311.19	0.086	0.017	1.938	1.010	0.066	330.95	0.692	0.178	1.070	1.392	0.149
311.51	0.101	0.020	1.897	1.013	0.076	332.17	0.710	0.190	1.061	1.412	0.142
311.94	0.123	0.023	1.806	1.021	0.091	332.92	0.723	0.198	1.051	1.436	0.136
312.32	0.139	0.027	1.829	1.023	0.103	333.98	0.736	0.209	1.047	1.445	0.131
312.33	0.139	0.027	1.795	1.023	0.101	334.77	0.743	0.217	1.043	1.439	0.124
312.72	0.160	0.030	1.722	1.032	0.113	336.18	0.761	0.235	1.043	1.454	0.122
312.93	0.176	0.032	1.640	1.043	0.122	337.59	0.772	0.250	1.037	1.443	0.112
313.14	0.179	0.033	1.671	1.039	0.123	341.21	0.815	0.299	1.026	1.513	0.097
313.57	0.198	0.037	1.625	1.046	0.132	345.64	0.851	0.364	1.017	1.528	0.077
313.88	0.214	0.039	1.579	1.054	0.139	347.59	0.865	0.394	1.010	1.536	0.067
314.43	0.237	0.043	1.544	1.062	0.149	348.44	0.872	0.410	1.011	1.538	0.065
314.57	0.251	0.044	1.477	1.076	0.152	350.18	0.884	0.440	1.006	1.551	0.056
314.91	0.260	0.047	1.507	1.074	0.159	354.59	0.912	0.525	1.002	1.559	0.041
315.56	0.288	0.052	1.460	1.089	0.170	356.79	0.926	0.570	0.996	1.602	0.031
316.16	0.318	0.057	1.394	1.110	0.177	357.62	0.929	0.589	0.998	1.562	0.030
316.88	0.346	0.062	1.349	1.127	0.181	358.21	0.934	0.604	0.998	1.599	0.029
317.51	0.368	0.067	1.332	1.138	0.187	362.15	0.953	0.701	0.999	1.572	0.020
318.18	0.402	0.072	1.272	1.171	0.191	363.44	0.960	0.733	0.996	1.601	0.015
319.65	0.442	0.082	1.249	1.188	0.194	367.35	0.978	0.844	0.996	1.579	0.006
320.45	0.468	0.088	1.218	1.208	0.193	370.10	0.991	0.933	1.001	1.490	0.005
321.30	0.493	0.095	1.196	1.228	0.192	372.09	1.000	1.000	1.000		0.000
Ethyl Propanoate (1) + Heptane (2)											
371.38	0.000	0.000		1.000	0.000	366.73	0.567	0.541	1.119	1.215	0.148
371.37	0.007	0.012	1.680	1.000	0.004	366.79	0.589	0.558	1.105	1.235	0.146
371.06	0.019	0.032	1.730	1.001	0.011	366.86	0.609	0.572	1.095	1.252	0.143
370.83	0.028	0.046	1.719	1.001	0.016	366.99	0.641	0.596	1.079	1.283	0.139
370.44	0.044	0.072	1.720	1.001	0.025	367.18	0.671	0.619	1.064	1.316	0.132
370.01	0.064	0.100	1.674	1.004	0.036	367.38	0.701	0.646	1.057	1.336	0.125
369.66	0.083	0.127	1.645	1.004	0.045	367.35	0.702	0.642	1.051	1.354	0.125
369.27	0.103	0.152	1.613	1.007	0.056	367.58	0.731	0.669	1.043	1.383	0.118
368.95	0.123	0.178	1.588	1.009	0.065	367.82	0.759	0.693	1.033	1.419	0.109
368.64	0.145	0.202	1.550	1.012	0.074	368.10	0.784	0.715	1.024	1.456	0.100
368.31	0.169	0.228	1.515	1.017	0.084	368.38	0.810	0.748	1.027	1.459	0.093
367.96	0.201	0.260	1.458	1.026	0.097	368.78	0.840	0.780	1.020	1.499	0.081
367.60	0.235	0.293	1.423	1.034	0.109	369.59	0.890	0.838	1.009	1.573	0.058
367.35	0.272	0.325	1.374	1.045	0.119	369.92	0.909	0.859	1.004	1.628	0.048
367.12	0.308	0.354	1.333	1.058	0.128	370.29	0.926	0.885	1.004	1.625	0.040
366.91	0.347	0.384	1.292	1.076	0.136	370.62	0.941	0.905	1.001	1.659	0.031
366.77	0.381	0.410	1.259	1.092	0.143	371.00	0.957	0.929	0.999	1.677	0.022
366.67	0.412	0.433	1.231	1.110	0.147	371.32	0.970	0.948	0.997	1.747	0.014
366.63	0.437	0.450	1.210	1.124	0.149	371.47	0.976	0.958	0.996	1.779	0.010
366.61	0.466	0.471	1.188	1.141	0.151	371.65	0.982	0.969	0.996	1.740	0.006
366.63	0.494	0.491	1.165	1.160	0.151	371.85	0.989	0.980	0.995	1.843	0.001
366.65	0.518	0.508	1.150	1.176	0.150	371.97	0.994	0.988	0.995	1.886	-0.001
366.69	0.543	0.525	1.132	1.196	0.149	372.09	1.000	1.000	1.000		0.000
Ethyl Propanoate (1) + Nonane (2)											
423.90	0.000	0.000		1.000	0.000	382.48	0.558	0.844	1.127	1.150	0.129
420.16	0.028	0.119	1.265	0.991	0.003	381.88	0.579	0.852	1.116	1.168	0.129
419.15	0.035	0.149	1.300	0.990	0.002	381.25	0.600	0.861	1.106	1.184	0.128
416.83	0.052	0.214	1.329	0.987	0.003	380.82	0.614	0.866	1.100	1.198	0.128

Table 7. continued

T/K	x_1	y_1	γ_1	γ_2	g^E/RT	T/K	x_1	y_1	γ_1	γ_2	g^E/RT
Ethyl Propanoate (1) + Nonane (2)											
413.92	0.073	0.289	1.361	0.985	0.009	379.62	0.658	0.882	1.081	1.243	0.125
411.45	0.094	0.348	1.349	0.988	0.017	378.76	0.690	0.892	1.069	1.286	0.124
404.81	0.153	0.495	1.368	0.985	0.035	378.10	0.716	0.901	1.060	1.314	0.119
401.77	0.184	0.554	1.369	0.985	0.045	377.45	0.742	0.910	1.052	1.345	0.114
399.45	0.215	0.594	1.332	0.996	0.059	376.85	0.768	0.918	1.043	1.391	0.109
396.97	0.247	0.636	1.317	1.002	0.069	375.55	0.828	0.938	1.025	1.494	0.090
394.95	0.276	0.670	1.304	1.005	0.077	374.95	0.857	0.947	1.017	1.573	0.079
393.06	0.310	0.700	1.273	1.015	0.085	374.51	0.878	0.954	1.014	1.602	0.070
391.09	0.346	0.729	1.249	1.026	0.094	373.88	0.910	0.966	1.009	1.658	0.054
388.94	0.389	0.759	1.224	1.046	0.106	373.32	0.937	0.976	1.007	1.673	0.039
387.65	0.420	0.777	1.200	1.062	0.112	372.76	0.964	0.985	1.003	1.883	0.026
385.45	0.473	0.806	1.172	1.089	0.120	372.33	0.985	0.993	1.003	2.129	0.014
384.38	0.505	0.820	1.151	1.114	0.124	372.09	1.000	1.000	1.000		0.000
383.43	0.531	0.833	1.139	1.129	0.126						

^aUncertainties u are: $u(T) = \pm 0.01$ K, $u(p) = \pm 0.02$ kPa, $u(x_1) = \pm 0.002$, and $u(y_1) = \pm 0.002$.

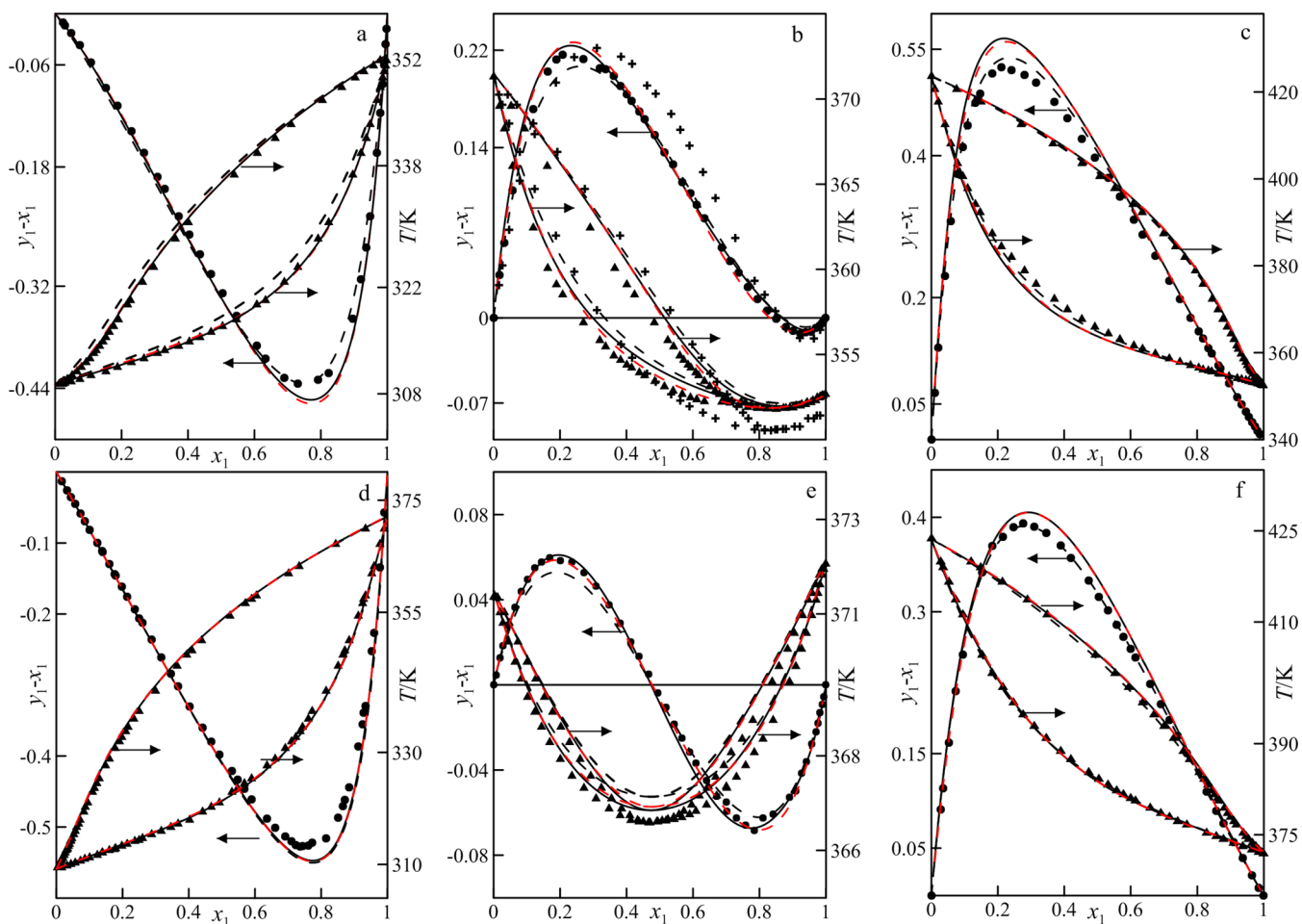


Figure 5. Plots of experimental iso-101.32 kPa VLE values and correlation curves (—, proposed model) for binaries: a, methyl propanoate (1) + pentane (2); b, methyl propanoate (1) + heptane (2); c, methyl propanoate (1) + nonane (2); d, ethyl propanoate (1) + pentane (2); e, methyl propanoate (1) + heptane (2); f, ethyl propanoate (1) + nonane (2). ●, (y_1-x_1) vs x_1 ; ▲, T vs x_1, y_1 ; black dashed line, UNIFAC; red dashed line, NRTL; +, values from ref 10.

with a difference, ~ 1 °C, in the temperature of that singular point. In general, we can attribute the differences to the greater precision of the values obtained now, owing to the higher degree of automation provided by the installations shown in Figure 1. By interpolating the data shown in Figure 5b and c, the position of

the azeotropic points ($x_{az}, T_{az}/K$) at a pressure of 101.32 kPa was calculated for the methyl propanoate + heptane (0.844, 351.86) and ethyl propanoate + heptane systems (0.481, 366.61), and their comparisons with those from literature²⁸ are presented in Table 8. Table 7 shows the values of the different thermodynamic

Table 8. Azeotropic Points^a and Comparison with Those from Literature and Estimated by UNIFAC

mixture	$x_{1,az}; T_{az}/K; P_{az}/kPa$	
	exptl	lit.
methyl propanoate (1) + heptane (2)	0.844; 351.86; 101.32	0.861; 350.61; 101.32 ^b <0.929; <352.75; 101.32 ^c
ethyl propanoate (1) + heptane (2)	0.481; 366.61; 101.32	0.465; 366.15; 101.32 ^c

^aUncertainties u are: $u(T_{az}) = \pm 0.01$ K, $u(P_{az}) = \pm 0.02$ kPa, $u(x_{az}) = \pm 0.003$. ^bReference 10. ^cReference 28.

quantities established for the iso- p VLE. Hence, the activity coefficients of the liquid phase γ_i were calculated by considering the nonideal nature of the vapor phase by the equation

$$x_i p_i^o \gamma_i = y_i p \frac{\hat{\phi}_i}{\phi_i^o} \exp \left[-\frac{v_i^o (p - p_i^o)}{RT} \right] \quad i = 1, 2 \quad (22)$$

where $\hat{\phi}_i$ is the fugacity coefficient of species i in solution, and ϕ_i^o and p_i^o are, respectively, the fugacity coefficient for pure i as a saturated vapor and the vapor pressure. The molar volumes of the pure compounds v_i^o were calculated at each equilibrium temperature with a modified version of Rackett's equation²⁹ and

the vapor pressures by Antoine's equation, with the parameters shown in Table 6. The ratio $(\hat{\phi}_i/\phi_i^o)$ is:

$$\frac{\hat{\phi}_i}{\phi_i^o} = \exp \left[\frac{B_{ii}(p - p_i^o) + p(1 - \gamma_i)^2(2B_{12} - B_{11} - B_{22})}{RT} \right] \quad i = 1, 2 \quad (23)$$

where the second virial coefficients for pure compounds B_{ii} and mixtures B_{ij} were obtained with the Tsonopoulos expressions.³⁰ Representations of γ_i and of Gibbs adimensional function g^E/RT are shown in Figure 6a–f. High values can be observed for the activity coefficients indicating strong deviations from the ideal solution, with a similar variation to that shown by the other mixing properties, increasing with the chain length of the hydrocarbon and decreasing with the increasing length of the alkanolic part of the propanoate. The experimental data shown in Table 6 were tested with the method proposed by Fredenslund³¹ to verify the thermodynamic consistency of iso- p VLE data; all of the systems fulfilled the global condition $\bar{\delta} = \sum_i |y_{i,exp} - y_{i,calc}|/N < 0.01$.

4.4. Treatment and Prediction of VLE Data and Mixing Properties. The values obtained for Gibbs excess function g^E (in $J \cdot mol^{-1}$), calculated from the data recorded in Table 7 for all of the systems, together with the h^E ^{6–8} and the c_p^E ¹⁵ for the binary system methyl propanoate + heptane, were used to

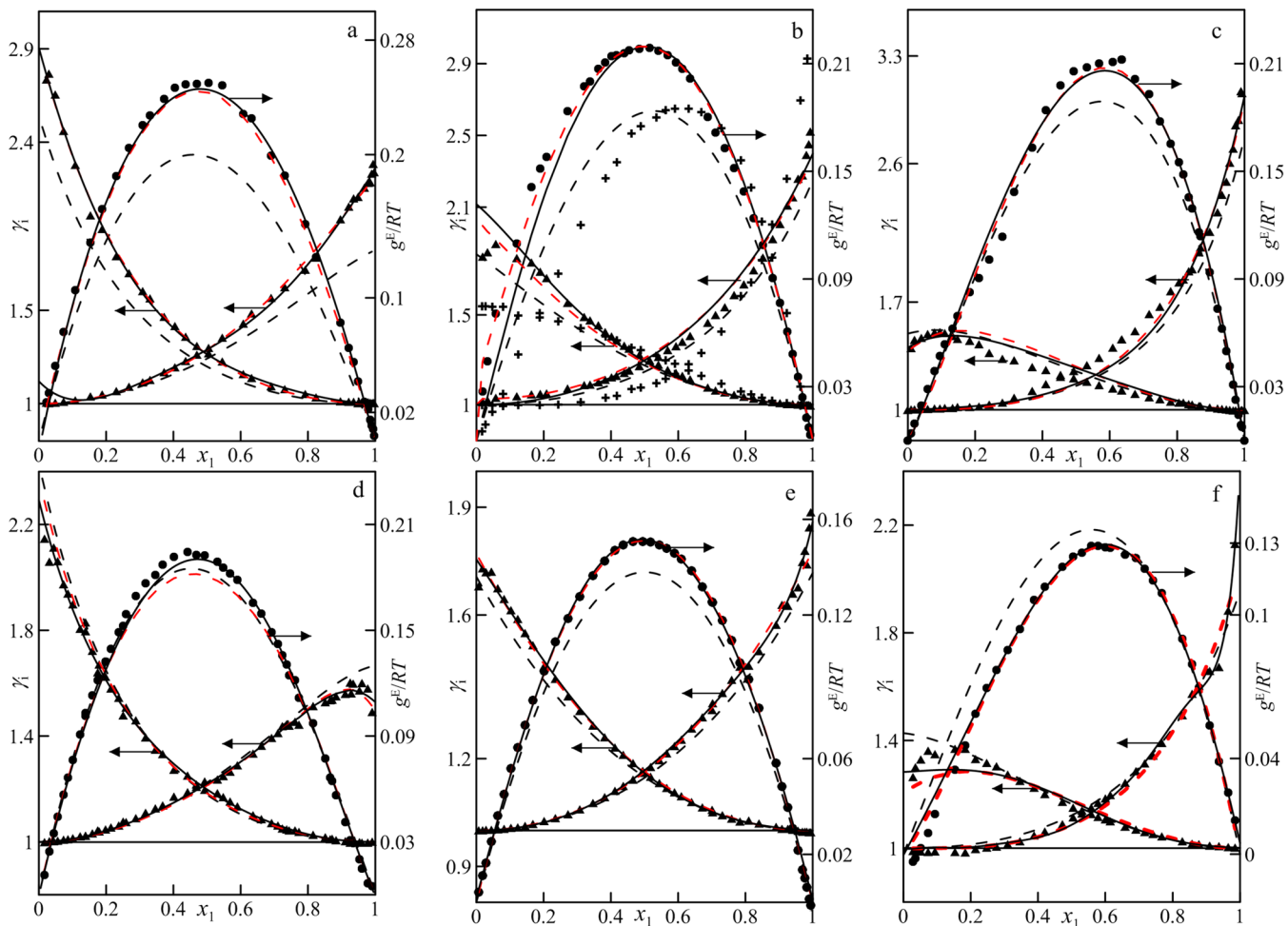


Figure 6. Plots of calculated iso-101.32 kPa VLE values and correlation curves (—, proposed model) for binaries: a, methyl propanoate (1) + pentane (2); b, methyl propanoate (1) + heptane (2); c, methyl propanoate (1) + nonane (2); d, ethyl propanoate (1) + pentane (2); e, ethyl propanoate (1) + heptane (2); f, ethyl propanoate (1) + nonane (2). ●, g^E/RT vs x_1 ; ▲, γ_i vs x_1 ; black dashed line, UNIFAC; red dashed line, NRTL; +, values from ref 10.

Table 9. Parameters of NRTL Obtained in the Simultaneous Correlation of Different Quantities (VLE, h^E , and c_p^E) of the Binaries Alkyl Propanoate + Alkane and Standard Deviations, s , for Each Property

	methyl propanoate			ethyl propanoate		
	pentane	heptane	nonane	pentane	heptane	nonane
Δg_{121}	$1.212 \cdot 10^2$	$-1.231 \cdot 10^1$	$-4.039 \cdot 10^1$	$4.236 \cdot 10^2$	8.404	1.128
Δg_{122}	$-1.268 \cdot 10^3$	$1.510 \cdot 10^3$	$6.264 \cdot 10^3$	$-2.172 \cdot 10^4$	$-6.452 \cdot 10^3$	$-1.955 \cdot 10^2$
Δg_{123}	$2.899 \cdot 10^1$	1.534	$1.100 \cdot 10^1$	$-6.111 \cdot 10^1$	9.142	$1.109 \cdot 10^1$
Δg_{211}	$-5.677 \cdot 10^2$	$2.416 \cdot 10^1$	$3.717 \cdot 10^1$	$-4.255 \cdot 10^2$	$9.875 \cdot 10^1$	-5.723
Δg_{212}	$1.527 \cdot 10^5$	$-1.388 \cdot 10^3$	$-4.914 \cdot 10^3$	$2.407 \cdot 10^4$	$5.425 \cdot 10^4$	$7.639 \cdot 10^2$
Δg_{213}	$3.486 \cdot 10^1$	-3.463	$-1.041 \cdot 10^1$	$6.010 \cdot 10^1$	$-3.532 \cdot 10^1$	-9.804
α	$1.6 \cdot 10^{-4}$	$8.0 \cdot 10^{-2}$	$2.0 \cdot 10^{-3}$	$-9.8 \cdot 10^{-2}$	$-2.8 \cdot 10^{-4}$	$9.8 \cdot 10^{-4}$
$s(\gamma_1)$	0.022	0.031	0.038	0.035	0.009	0.029
$s(\gamma_2)$	0.022	0.037	0.044	0.016	0.018	0.027
$s(g^E/RT)$	0.005	0.005	0.005	0.006	0.002	0.004
$s(h^E)$ ($T = 298.15$ K)	20	7	24	10	5	8
$s(h^E)$ ($T = 318.15$ K)		8	16		16	10
$s(c_p^E)$		$1.5 \cdot 10^{-1}$				

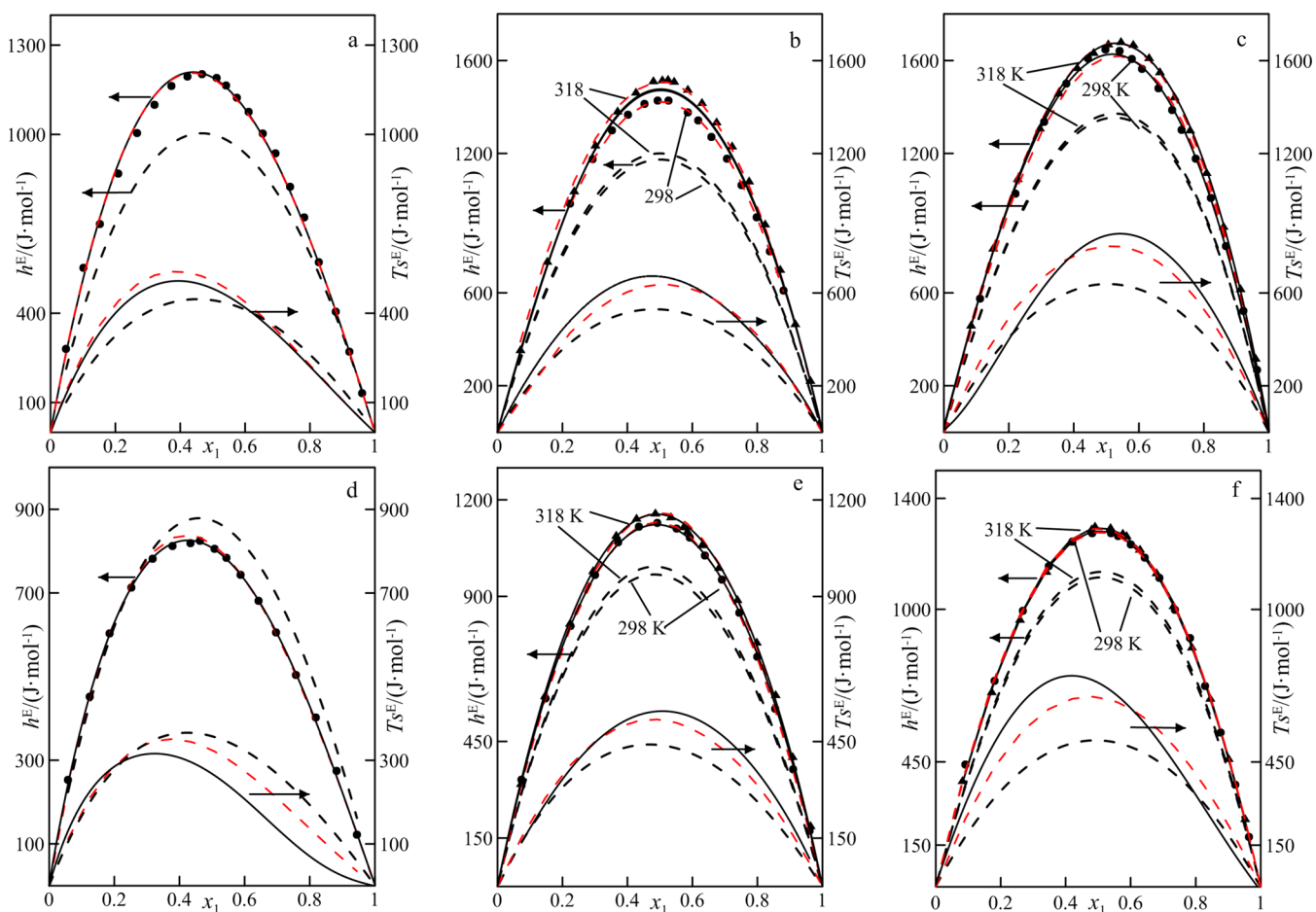


Figure 7. Plots of experimental h^E values measured at 298.15 K (●) and 318.15 K (▲), and correlation curves (—, proposed model) for the binaries: a, methyl propanoate (1) + pentane (2); b, methyl propanoate (1) + heptane (2); c, methyl propanoate (1) + nonane (2); d, ethyl propanoate (1) + pentane (2); e, ethyl propanoate (1) + heptane (2); f, ethyl propanoate (1) + nonane (2). Black dashed line, UNIFAC; red dashed line, NRTL.

correlate the properties for each system. The two models described in Section 3 were used in the procedure, the one defined by eq 2 with the coefficients of eq 4 and its corresponding derivatives and the NRTL model, eq 14. Because of the polynomial form of the proposed model, two procedures can be used to correlate the thermodynamic quantities mentioned.

(a) The first, already used in previous works,² which simultaneously correlates the different quantities, taking into

consideration the expressions established in Section 3. This method can also be applied to the NRTL model. For this purpose it is recommendable to use a robust algorithm that minimizes a global objective function that includes the different local minima of each quantity, in other words:

$$OF = c_1 s(\ln \gamma_1) + c_2 s(\ln \gamma_2) + c_3 s(h^E) \quad (24)$$

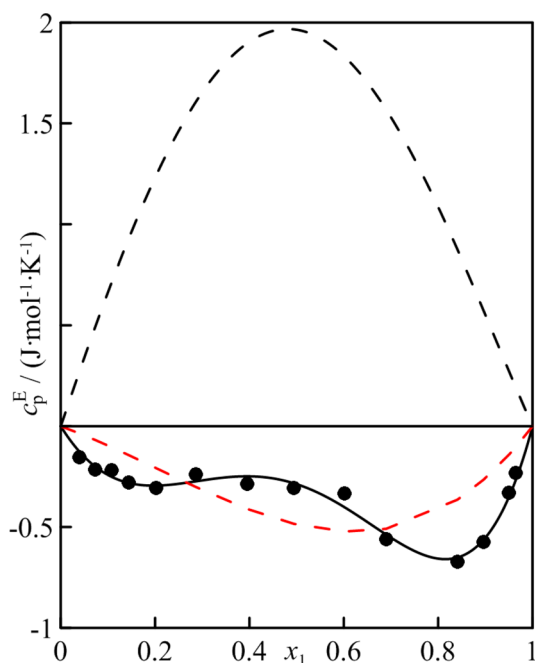


Figure 8. Plots of c_p^E vs x_1 at 298.15 K (●) and correlation curves (—, proposed model) for binary methyl propanoate (1) + heptane (2). Black dashed line, UNIFAC; red dashed line, NRTL.

where the c_i are weighting coefficients for the different quantities treated and are calculated in the correlation procedure. To carry out the correlation, a genetic algorithm implemented in Matlab was used that produced good results for both models. The $s(y^E)$ were defined by eq 20.

For this case, the k parameters (k_h^{21} and k_g^{21}) of the proposed model were determined together with the g_{ij} coefficients in the same procedure of fit. The results obtained for the parameters of the NRTL model are shown in Table 9 and graphically represented in Figures 5 to 8; they show a good correlation for the iso- p VLE and h^E data but not for the c_p^E (Figure 8), since the rigidity of the model prevents the inflections shown by the

Table 11. Activity Coefficients at Infinite Dilution Obtained by Two Models (eqs 12, 13, and 18) and Comparison with Those Estimated by UNIFAC

	methyl propanoate			ethyl propanoate		
	pentane	heptane	nonane	pentane	heptane	nonane
γ_1^∞	2.968 ^a	2.099 ^a	1.353 ^a	2.292 ^a	1.749 ^a	1.304 ^a
	2.913 ^b	2.054 ^b	1.380 ^b	2.379 ^b	1.772 ^b	1.207 ^b
	2.482 ^c	1.838 ^c	1.495 ^c	2.242 ^c	1.706 ^c	1.428 ^c
γ_2^∞	2.258 ^a	2.646 ^a	3.049 ^a	1.529 ^a	1.899 ^a	2.251 ^a
	2.217 ^b	2.217 ^b	2.427 ^b	3.011 ^b	1.498 ^b	2.047 ^b
	1.814 ^c	2.251 ^c	2.776 ^c	1.706 ^c	1.717 ^c	1.956 ^c

^aCalculated by eqs 12 and 13. ^bCalculated by eq 18. ^cEstimated by UNIFAC.

experimental points. Table 9 shows that the nonrandomness parameter, α , obtained in the correlation procedure is optimized to nonregular (even negative) values, very different to the authors' proposal for these mixtures ($\alpha = 0.3$ to 0.47).

(b) The second fitting procedures are only applicable to the proposed model, permitting partial correlations or by steps, that can be shown by the succession (x, T, c_p^E [eq 6]) \rightarrow (x, T, h^E [eq 5]) \rightarrow (x, T, g^E [eq 2]). This method presents certain advantages over simultaneous correlation, since the partial fit of each property needs a simple objective function, such as that of eq 20, and a smaller number of parameters are determined in each step. For these mixtures, the k_h^{21} value obtained in the fit of (x, h^E) [see refs 6 to 8], is fixed and introduced in the second step. Regression of the experimental data to the model generated the values shown in Table 10. However, application of the simultaneous correlation procedure indicated in (a) for the proposed model with the OF of eq 24 gave similar results. The corresponding representations are depicted in Figures 5 to 8, showing good quality reproductions of the behavior of all systems, including those of c_p^E .

The UNIFAC³ estimates for the different properties were generally of poor quality. The Gibbs function and the activity coefficients were underestimated in nearly all cases, with values lower than experimental ones, except for the ethyl propanoate + nonane system. Predictions for the mixing enthalpies are not

Table 10. Parameters for the Proposed Model, Obtained by Step-by-Step Correlation Procedure of Different Quantities (VLE, h^E , and c_p^E) of the Binaries Alkyl Propanoate + Alkane and Standard Deviations, s , for Each Property

	methyl propanoate			ethyl propanoate		
	pentane	heptane	nonane	pentane	heptane	nonane
k_G	1.375	0.851	0.790	1.539	0.855	3.332
k_H	1.126	1.431	1.741	0.961	1.222	1.486
k_C		1.103				
G_{00}		$1.851 \cdot 10^5$	$6.097 \cdot 10^4$		$-6.121 \cdot 10^5$	$3.441 \cdot 10^5$
G_{10}		$-6.906 \cdot 10^5$	$-1.506 \cdot 10^6$		$2.025 \cdot 10^6$	$-1.799 \cdot 10^6$
G_{20}		$8.600 \cdot 10^5$	$3.367 \cdot 10^5$		$-2.521 \cdot 10^6$	$1.643 \cdot 10^6$
G_{01}	$4.227 \cdot 10^3$	$5.624 \cdot 10^3$	$9.701 \cdot 10^3$	$4.357 \cdot 10^3$	$9.918 \cdot 10^3$	$5.033 \cdot 10^3$
G_{11}	$1.327 \cdot 10^3$	$-1.878 \cdot 10^3$	$1.026 \cdot 10^2$	$-2.686 \cdot 10^3$	$-1.691 \cdot 10^4$	$6.288 \cdot 10^3$
G_{21}	$-4.209 \cdot 10^2$	$-2.595 \cdot 10^3$	$1.873 \cdot 10^3$	$9.096 \cdot 10^2$	$1.811 \cdot 10^4$	$-9.036 \cdot 10^3$
G_{02}	-1.355	$-1.246 \cdot 10^1$	$-2.105 \cdot 10^1$	$-3.640 \cdot 10^1$	$-1.821 \cdot 10^1$	$-6.589 \cdot 10^1$
G_{12}	$-1.479 \cdot 10^1$	$1.155 \cdot 10^1$	$7.553 \cdot 10^1$	$-1.563 \cdot 10^1$	$3.224 \cdot 10^1$	$-1.947 \cdot 10^1$
G_{22}	$6.518 \cdot 10^1$	$9.969 \cdot 10^{-1}$	$1.042 \cdot 10^1$	$6.891 \cdot 10^{-1}$	$-3.021 \cdot 10^1$	$2.086 \cdot 10^1$
$s(\gamma_1)$	0.024	0.012	0.042	0.034	0.013	0.028
$s(\gamma_2)$	0.014	0.022	0.063	0.029	0.023	0.019
$s(g^E/RT)$	0.003	0.002	0.006	0.004	0.002	0.005
$s(h^E)$ ($T = 298$ K)	15	16	17	6	5	9
$s(h^E)$ ($T = 318$ K)		25	13		5	8
c_p^E		$3 \cdot 10^{-2}$				

adequate either, showing important discrepancies with experimental values (Figure 7). The curve of $c_p^E(x)$ for the binary methyl propanoate + heptane estimated by UNIFAC is of opposite sign to the experimental. The database we are generating for these mixtures incorporates the γ_i^∞ for their interest in theoretical and practical studies. In the field of chemical engineering, there is interest to know the behavior of the highly diluted solutions to evaluate the recovery or separation capability of the components. Thus, the γ_i^∞ were calculated using the two correlation models and are shown in Table 11, showing certain differences with those obtained by UNIFAC. The variation of said coefficients with the nature of the compounds is notorious, especially of γ_2^∞ with "n" attributable to ester associative effects which are smaller than with other short chain alkanate.^{4,5} Although the models used for g^E are empirical in their development, the γ_i^∞ obtained from them can be used to check the reliability of the model.

With the different models (correlative and predictive) the behavior of the energy function Ts^E was estimated, and the results are shown in Figure 7. The entropic function increases with the saturated chain length and diminishes with an increase in the alkanolic part of the ester. In other words, the variations occur in the same direction as those observed for the other mixing properties, interpreted in Section 4.1.

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Notes

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