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Measurements of the Excess Properties and Vapor−Liquid Equilibria at 101.32 kPa for Mixtures of Ethyl Ethanoate + Alkanes (from C_5 to C_{10})[†]

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This work presents experimental values for the excess volumes (V_m^E) at 291.15, 298.15, 318.15, and 328.15 K; excess enthalpies (H_m^E) at 291.15, 298.15, and 318.15 K; and vapor−liquid equilibria (VLE) at 101.32 kPa for mixtures of ethyl ethanoate with each of six alkanes (from pentane to decane). The results for the six mixtures show that the thermal coefficient $(\partial V_m^E/\partial T)_p$ is positive and that $(\partial H_m^E/\partial T)_p$ presents changes in the sign. The Fredenslund method was applied to establish the thermodynamic consistency of the VLE data. Of the six systems considered here, only two, ethyl ethanoate + hexane and ethyl ethanoate + heptane, form minimum-boiling azeotropes, with coordinates (x_{az}, T_{az}/K) of (0.339, 338.15) and (0.834, 349.99), respectively. Simultaneous correlations carried out with the VLE and H_m^E data using a polynomic model with temperature-dependent coefficients were found to be acceptable. Application of two different versions of the UNIFAC model for the VLE data, one by Hansen et al. (*Ind. Eng. Chem. Res.* **1991**, *30*, 2355) and the other by Gmehling et al. (*Ind. Eng. Chem. Res.* **1993**, *32*, 178), gave similar estimations for the six systems, which we consider to be acceptable. The second method gave good predictions of H_m^E.

Introduction

Several years ago, our research team started a project on solutions of alkyl esters (especially with alkanols) because of their importance in biofuel studies. Some results on the mixing properties of alkyl esters + alkanols, including studies on vapor−liquid equilibria (VLE) modeling/prediction (through the group contribution methods ASOG and UNIFAC) have already been published.[1−3] In the area of phase equilibria, even though VLE studies of primary systems such as alkanols + alkanes and esters + alkanes are necessary, they have not been explored. Numerous studies have published excess properties of ester + alkane mixtures determined isothermally at 298.15 K,[4,5] but there are few studies of this nature for other binary systems. The present work extends the database of the excess properties and isobaric VLE for these compounds. VLE data and other properties of methanoates + alkanes have been published previously,[6,7] and further articles will report our studies of the same family of compounds.

In an attempt to systematize the research, this work shows experimental results for the six systems ethyl ethanoate + alkane (C_5 to C_{10}). For some of these systems, H_m^E and V_m^E data at a temperature of 298.15 K have been reported in the literature.[5,9] For the mixtures of ethyl ethanoate with alkanes having odd numbers of carbon atoms, data on H_m^E and V_m^E at 318.15 K are available in the literature.[8] For VLE data, measurements were made at constant pressure for systems containing the same ester mixed with C_6,[10] C_8,[11] and C_9[12] that can be used for comparison. Other articles[13−16] present isothermal VLE data for some of the mixtures chosen.

Another objective of the proposed project pertains to data treatment both to correlate and to estimate or predict the properties, and in the latter case, two versions of the UNIFAC group contribution method were used.[17,18] Correlation was done by applying the mathematical model proposed previously by our research group[19,20] in which the excess Gibbs function $G_m^E = G_m^E[z(x),T]$ is described as a function of the *effective volumetric fraction*, which is adequate for stepwise or simultaneous correlation of different thermodynamic properties over a wide range of pressures and temperatures.

Experimental Section

Materials. The mass-fraction purities of ethyl ethanoate and the alkanes obtained from Aldrich for use in the experimental part of this work were greater than 0.99. Before use, all of the products were degasified by ultrasound for several hours and then passed through a molecular sieve (0.3 nm, Fluka). The quality of the products was verified by measuring their normal boiling points $T_{b,i}^\circ$, isobaric thermal expansivities α, densities $\rho^{298.15K}$ and refractive indices $n_D^{298.15K}$. The experimental values were compared with published values as shown in Table 1, and the differences obtained were not significant.

Methods. The experimental isobaric VLE data were measured with a small-volume device described previously[24] that was modified by the installation of auxiliary equipment to improve its performance as indicated below. A 60 cm^3 glass ebulliometer in which both phases circulated continuously was used. Pressure was controlled with a controller/calibrator (model PPC2, Desgranges & Huot, France) that maintained the pressure at (101.32 ± 0.02) kPa for the duration of the experiment. Equilibrium between the two phases was reached after approximately 15 min, maintaining p and T constant. Temperatures were recorded with a digital thermometer (Model 6800, Comarks Electronics Ltd.) that was regularly calibrated according to ITS-90 with an

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Table 1. Properties of the Pure Compounds at 101.32 kPa

	$T^{\circ}_{b,i}$/K		$10^3\cdot\alpha$/K^{-1}		$\rho^{298.15K}$/kg·m^{-3}		$n_D^{298.15K}$	
compound	exptl	lit	exptl	lit	exptl	lit	exptl	lit
$CH_3COOC_2H_5$	350.15	350.26[c]	1.41	1.44[b] 1.41[d]	894.40	894.24[a] 894.55[c]	1.3697	1.3700[a] 1.3698[c]
$CH_3(CH_2)_3CH_3$	309.30	309.22[c]	1.57	1.66[d]	621.35	621.39[c] 621.10[d]	1.3545	1.3547[c] 1.3549[d]
$CH_3(CH_2)_4CH_3$	341.88	341.93[b] 341.89[c]	1.43	1.39[c] 1.40[d]	654.84	654.59[b] 654.81[c]	1.3723	1.3724[b] 1.37226[c]
$CH_3(CH_2)_5CH_3$	371.56	371.18[b] 371.58[c]	1.28	1.29[d]	679.48	679.27[b] 679.51[c]	1.3852	1.3853[b] 1.3851[c]
$CH_3(CH_2)_6CH_3$	398.83	398.65[b] 398.82[c]	1.18	1.16[c] 1.19[d]	698.60	698.39[b] 698.49[c]	1.3952	1.3951[b] 1.39505[c]
$CH_3(CH_2)_7CH_3$	423.94	423.66[b] 423.95[c]	1.11	1.12[d]	713.85	713.85[b] 713.81[c]	1.4031	1.4030[b] 1.40311[c]
$CH_3(CH_2)_8CH_3$	447.30	446.90[b] 447.27[c]	1.05	1.05[c] 1.07[d]	726.20	726.19[b] 726.25[c]	1.4096	1.4098[b] 1.4097[c]

[a] Data from ref 5. [b] Data from ref 19. [c] Data from ref 21. [d] Data from ref 22.

uncertainty in the measurement of ± 20 mK identical to that reported by the manufacturer. The same apparatus was also used to measure the vapor pressures of the pure compounds.

After equilibrium had been reached, the phase compositions were determined indirectly by densimetry. For each of the ethyl ethanoate (1) + alkane (2) systems, synthetic mixtures were prepared at known compositions $x_1 \pm 0.0002$, and values of ρ with an uncertainty of ± 0.02 kg·m^{-3} were measured at T = 298.15 K in a DMA-55 Anton Paar digital densimeter. The pertinent data were correlated using the linear expression $\rho(x_1) = [(\rho_1 - \rho_2)x_1 + \rho_2] - [x_1(1 - x_1)(ax_1^2 + bx_1 + c)]$, where ρ, ρ_1, and ρ_2 are the densities of the mixture, the ester, and the pure alkane, respectively. For the mixtures of two phases, the values of ρ and the compositions x_1 and y_1 of the liquid and vapor phases, respectively, were measured, yielding the set of values (p/kPa ± 0.02, T/K ± 0.02, $x_1 \pm 0.002$, $y_1 \pm 0.002$) for each mixture. The values of density and composition could also be used to calculate the excess volumes V_m^E with an uncertainty of ± $2\cdot10^9$ m^3·mol^{-1}, while the compositions x_1, as indicated previously, had an uncertainty of ± $2\cdot10^{-4}$.

The n_D values of the pure substances were measured with an Abbe refractometer (model 320, Zuzi) that had a reading error of ± 0.0002 units and was thermostatted to maintain a constant working temperature by circulating water from a Heto Birkerod water bath, which provided excellent control of the temperature in the apparatus within ± 0.02 K of the selected value.

The excess enthalpies H_m^E were measured directly at the three temperatures chosen, T = (291.15, 298.15, and 318.15) K, in a Calvet microcalorimeter (model MS80D, SETARAM, Lyon, France) that was electrically calibrated at each temperature by

Table 2. Densities ρ and Excess Molar Volumes V_m^E for Binary Systems of Ethyl Ethanoate (1) + Alkane (2) at Four Different Temperatures

x_1	$\frac{\rho}{kg\cdot m^3}$	$\frac{10^9\cdot V_m^E}{m^3\cdot mol^{-1}}$	x_1	$\frac{\rho}{kg\cdot m^3}$	$\frac{10^9\cdot V_m^E}{m^3\cdot mol^{-1}}$	x_1	$\frac{\rho}{kg\cdot m^3}$	$\frac{10^9\cdot V_m^E}{m^3\cdot mol^{-1}}$
				T = 291.15 K				
				Ethyl Ethanoate (1) + Pentane (2)				
0.0000	628.22	0	0.3916	721.01	646	0.8582	856.32	215
0.0126	630.77	72	0.4566	738.23	637	0.8961	868.57	152
0.0577	640.44	242	0.5296	758.09	615	0.9693	892.55	50
0.0922	648.09	340	0.5916	775.48	577	1.0000	902.88	0
0.1813	668.69	505	0.6517	792.81	524			
0.2507	685.25	607	0.7164	812.13	435			
0.3232	703.25	659	0.7788	831.21	348			
				Ethyl Ethanoate (1) + Hexane (2)				
0.0000	661.17	0	0.3518	725.37	923	0.8980	868.30	318
0.0165	663.70	92	0.4166	739.37	947	0.9604	888.98	143
0.0655	671.62	306	0.5519	770.91	905	0.9833	896.93	64
0.1077	678.72	464	0.6225	788.69	839	1.0000	902.88	0
0.1823	692.02	669	0.6795	803.74	768			
0.1962	694.54	709	0.7429	821.35	660			
0.2716	709.09	827	0.8048	839.41	535			
				Ethyl Ethanoate (1) + Heptane (2)				
0.0000	685.28	0	0.4396	753.49	1087	0.8631	856.84	517
0.0161	687.34	61	0.5126	768.17	1081	0.9105	872.00	344
0.0572	692.44	271	0.5792	782.54	1044	0.9718	892.61	133
0.1159	700.33	493	0.6414	796.91	977	1.0000	902.88	0
0.2057	713.27	778	0.7006	811.50	889			
0.2894	726.55	951	0.7555	825.89	785			
0.3673	740.00	1048	0.8141	842.35	640			
				Ethyl Ethanoate (1) + Octane (2)				
0.0000	704.13	0	0.3723	750.35	1112	0.7945	836.98	812
0.0296	707.15	127	0.4427	761.76	1163	0.8400	849.83	666
0.0628	710.48	301	0.5131	774.24	1166	0.8950	866.53	471
0.1163	716.36	507	0.5744	785.94	1152	0.9304	878.05	331
0.1605	721.46	667	0.6332	798.14	1099	0.9523	885.46	243
0.2056	727.01	797	0.6886	810.54	1023	1.0000	902.88	0
0.2901	738.23	994	0.7414	823.25	927			

Table 2. Continued

x_1	$\frac{\rho}{\mathrm{kg \cdot m^3}}$	$\frac{10^9 \cdot V_\mathrm{m}^\mathrm{E}}{\mathrm{m^3 \cdot mol^{-1}}}$	x_1	$\frac{\rho}{\mathrm{kg \cdot m^3}}$	$\frac{10^9 \cdot V_\mathrm{m}^\mathrm{E}}{\mathrm{m^3 \cdot mol^{-1}}}$	x_1	$\frac{\rho}{\mathrm{kg \cdot m^3}}$	$\frac{10^9 \cdot V_\mathrm{m}^\mathrm{E}}{\mathrm{m^3 \cdot mol^{-1}}}$
Ethyl Ethanoate (1) + Nonane (2)								
0.0000	719.20	0	0.4659	771.77	1235	0.8502	852.64	707
0.0328	721.88	162	0.5694	788.99	1228	0.8954	866.20	534
0.0796	726.00	355	0.6015	794.91	1203	0.9307	877.58	388
0.1292	730.54	563	0.6514	804.70	1150	0.9918	899.59	61
0.2225	740.13	853	0.7041	815.84	1079	1.0000	902.88	0
0.3076	750.00	1047	0.7547	827.59	970			
0.3932	761.25	1161	0.8076	840.96	834			
Ethyl Ethanoate (1) + Decane (2)								
0.0000	731.22	0	0.5149	783.83	1295	0.8914	864.68	581
0.0174	732.37	95	0.5781	793.79	1281	0.9318	877.69	395
0.0789	736.87	360	0.6446	805.51	1225	0.9794	894.70	141
0.1457	742.14	633	0.7051	817.52	1126	1.0000	902.88	0
0.2494	751.47	967	0.7648	830.70	1004			
0.3508	762.27	1168	0.8069	841.06	880			
0.4382	773.02	1272	0.8553	854.05	722			
$T = 298.15$ K								
Ethyl Ethanoate (1) + Pentane (2)								
0.0000	621.35	0	0.3576	703.99	771	0.8245	836.93	328
0.0260	626.34	195	0.4301	722.92	752	0.8825	855.30	242
0.0607	633.60	352	0.4703	733.71	726	0.9342	872.31	132
0.0897	639.94	443	0.5276	749.44	677	0.9896	890.79	30
0.1609	655.94	624	0.6553	785.76	550	1.0000	894.40	0
0.2315	672.51	735	0.7126	802.69	480			
0.3028	690.12	761	0.7725	820.79	405			
Ethyl Ethanoate (1) + Hexane(2)								
0.0000	654.90	0	0.4440	738.30	982	0.8292	838.80	487
0.0704	666.20	301	0.4935	749.50	986	0.8612	848.70	397
0.1270	675.70	513	0.5355	759.40	966	0.9233	868.50	230
0.1930	687.40	704	0.5869	772.00	920	0.9469	876.30	161
0.2383	695.90	790	0.6255	781.80	875	1.0000	894.40	0
0.2909	706.10	875	0.7012	801.90	760			
0.3466	717.40	933	0.7532	816.40	664			
Ethyl Ethanoate (1) + Heptane (2)								
0.0000	679.48	0	0.3171	724.70	1030	0.7780	824.17	783
0.0409	684.35	230	0.3703	733.90	1091	0.8302	839.02	636
0.0568	686.42	289	0.4203	743.04	1121	0.8787	853.80	464
0.1196	694.72	538	0.4911	756.80	1128	0.9206	867.23	306
0.1493	698.85	638	0.5587	770.85	1107	0.9879	890.20	37
0.2079	707.39	805	0.6169	783.73	1066	1.0000	894.40	0
0.2587	715.20	925	0.6668	795.46	1005			
0.2981	721.51	1006	0.7270	810.54	899			
Ethyl Ethanoate (1) + Octane (2)								
0.0000	698.60	0	0.4622	758.48	1216	0.7913	828.60	836
0.0485	703.30	258	0.4977	764.69	1217	0.8335	840.20	708
0.0998	708.80	456	0.5598	776.23	1196	0.8686	850.50	579
0.1711	716.90	713	0.6729	799.80	1072	0.9039	861.40	441
0.2518	727.02	928	0.6548	795.80	1097	0.9578	879.30	202
0.3198	736.29	1071	0.6865	802.90	1047	1.0000	894.40	0
0.3814	745.42	1155	0.7550	819.20	929			
Ethyl Ethanoate (1) + Nonane (2)								
0.0000	713.85	0	0.4737	766.60	1272	0.8024	832.16	864
0.0652	719.20	315	0.5212	774.12	1279	0.8428	843.01	733
0.1102	723.17	510	0.5875	785.50	1263	0.8654	849.38	659
0.1906	730.94	798	0.6305	793.54	1227	0.9419	873.16	352
0.2667	739.14	1010	0.6743	802.32	1170	0.9564	878.07	287
0.3377	747.65	1150	0.7212	812.53	1074	1.0000	894.40	0
0.4128	757.70	1230	0.7670	823.20	974			
Ethyl Ethanoate (1) + Decane (2)								
0	726.20	0	0.4873	773.59	1342	0.8179	836.50	871
0.0319	728.30	170	0.5417	781.58	1341	0.8516	845.40	763
0.1165	734.60	518	0.6031	791.53	1302	0.8865	855.40	622
0.2048	741.90	850	0.6469	799.34	1248	0.9207	866.10	454
0.2835	749.30	1079	0.6957	808.80	1163	0.9604	879.50	250
0.3475	756.10	1206	0.7407	818.30	1068	1	894.40	0
0.4252	765.35	1302	0.7800	827.20	979			
$T = 318.15$ K								
Ethyl Ethanoate (1) + Hexane (2)								
0.0000	636.50	0	0.3976	707.00	1131	0.7984	806.00	643
0.0336	641.50	191	0.4495	718.10	1138	0.8419	818.80	526
0.0764	648.10	407	0.5054	730.60	1117	0.8854	832.20	383
0.1448	659.30	675	0.5551	742.20	1075	0.9305	846.40	250
0.2606	679.90	976	0.6085	755.10	1023	1.0000	869.60	0
0.2760	682.80	1003	0.7048	779.90	864			
0.3316	693.50	1093	0.7523	792.90	758			

Table 2. Continued

x_1	ρ / $\mathrm{kg \cdot m^3}$	$10^9 \cdot V_m^E$ / $\mathrm{m^3 \cdot mol^{-1}}$	x_1	ρ / $\mathrm{kg \cdot m^3}$	$10^9 \cdot V_m^E$ / $\mathrm{m^3 \cdot mol^{-1}}$	x_1	ρ / $\mathrm{kg \cdot m^3}$	$10^9 \cdot V_m^E$ / $\mathrm{m^3 \cdot mol^{-1}}$
Ethyl Ethanoate (1) + Heptane (2)								
0.0000	662.06	0	0.3991	719.02	1263	0.7248	787.48	1024
0.0530	668.20	301	0.4184	722.43	1279	0.7652	797.95	909
0.0902	672.90	453	0.4793	733.70	1299	0.7914	804.97	832
0.1685	683.15	774	0.5280	743.25	1290	0.8486	821.19	628
0.2326	692.18	986	0.5785	753.70	1256	0.9067	838.76	403
0.2439	693.85	1016	0.6277	764.50	1192	0.9554	854.25	221
0.2981	702.14	1139	0.6774	775.92	1121	1.0000	869.60	0
Ethyl Ethanoate (1) + Octane (2)								
0.0000	682.16	0	0.4875	743.04	1381	0.8487	821.51	736
0.0340	685.37	168	0.5678	757.24	1360	0.8943	834.53	576
0.1080	692.60	545	0.6088	765.10	1323	0.9320	846.34	386
0.1961	702.19	897	0.6633	776.23	1250	0.9762	860.93	168
0.2859	713.24	1139	0.7123	786.92	1169	1.0000	869.60	0
0.3635	723.80	1286	0.7640	799.14	1040			
0.4203	732.23	1351	0.8086	810.54	893			
Ethyl Ethanoate (1) + Nonane (2)								
0.0000	698.09	0	0.5311	756.19	1451	0.8955	835.04	606
0.0372	700.83	216	0.5965	767.10	1406	0.9360	847.56	392
0.1287	708.30	662	0.6714	781.02	1304	0.9808	862.66	126
0.2206	717.00	980	0.7111	789.15	1220	1.0000	869.60	0
0.3125	726.84	1222	0.7598	799.77	1110			
0.3941	736.68	1373	0.8122	812.28	956			
0.4659	746.38	1444	0.8596	824.75	774			
Ethyl Ethanoate (1) + Decane (2)								
0.0000	710.90	0	0.4391	749.04	1444	0.8204	815.00	977
0.0117	711.52	91	0.5160	758.96	1487	0.8538	823.50	841
0.0758	715.68	416	0.5314	761.13	1483	0.8886	833.00	687
0.1539	721.34	754	0.5878	769.54	1456	0.9198	842.30	516
0.2456	728.94	1065	0.6448	778.92	1397	0.9553	853.80	294
0.2848	732.56	1165	0.6940	787.77	1327	1.0000	869.60	0
0.3468	738.71	1304	0.7127	791.38	1289			
0.3714	741.31	1351	0.7829	806.20	1101			
$T = 328.15$								
Ethyl Ethanoate (1) + Hexane (2)								
0.0000	627.00	0	0.4318	703.25	1246	0.8221	800.90	627
0.0433	633.20	287	0.4918	716.30	1233	0.8723	815.80	485
0.0847	639.60	483	0.5567	731.20	1175	0.9135	828.60	345
0.1691	653.40	806	0.6075	743.40	1109	0.9832	851.30	88
0.2349	664.80	1007	0.6523	754.60	1032	1.0000	857.17	0
0.3070	678.00	1174	0.7238	773.40	872			
0.3708	690.60	1228	0.7577	782.70	785			
Ethyl Ethanoate (1) + Heptane (2)								
0.0000	653.60	0	0.4880	725.11	1394	0.8717	815.94	614
0.0084	654.45	70	0.5492	737.13	1361	0.9217	831.14	403
0.1044	665.69	593	0.6210	752.34	1268	0.9731	847.90	148
0.1911	676.99	943	0.6655	762.36	1190	1.0000	857.17	0
0.2817	690.09	1187	0.7209	775.45	1085			
0.3479	700.46	1312	0.7755	789.39	923			
0.4230	713.16	1391	0.8274	803.37	762			
Ethyl Ethanoate (1) + Octane (2)								
0.0000	674.15	0	0.5234	739.31	1458	0.8822	819.28	658
0.0441	678.00	278	0.5735	748.22	1429	0.9270	832.83	428
0.1138	684.70	633	0.6354	760.07	1359	0.9737	848.01	167
0.2084	694.85	1008	0.6861	770.65	1257	1.0000	857.17	0
0.2915	704.80	1256	0.7435	783.45	1127			
0.3741	715.90	1403	0.7958	796.07	979			
0.4415	725.91	1457	0.8407	807.86	807			
Ethyl Ethanoate (1) + Nonane (2)								
0.0000	690.40	0	0.5377	747.63	1523	0.9507	840.17	345
0.0202	691.70	155	0.6125	759.98	1460	0.9876	852.64	101
0.1246	699.90	670	0.7233	781.10	1271	1.0000	857.17	0
0.2225	708.81	1035	0.7593	788.80	1186			
0.3109	717.88	1300	0.8102	800.56	1037			
0.3923	727.35	1461	0.8505	810.90	861			
0.4644	736.84	1524	0.8934	822.54	685			
Ethyl Ethanoate (1) + Decane (2)								
0.0000	703.34	0	0.5551	755.09	1545	0.9511	840.13	372
0.0347	705.37	206	0.6186	764.72	1493	1.0000	857.17	0
0.1351	711.99	706	0.6774	774.65	1409			
0.2340	719.58	1101	0.7271	783.92	1308			
0.3322	728.47	1372	0.7735	793.40	1189			
0.4166	737.37	1510	0.8619	814.12	883			
0.4853	745.64	1554	0.9041	825.66	672			

applying a Joule effect using a Setaram EJ3 power source, which produced thermograms similar to the mixing processes when different powers were applied to a special calibration cell. A differential assembly was used for the calorimetric process in all cases. Data were recorded and treated using the commercial software SETSOFT by Setaram. The necessary temperature modifications were made between the temperatures recorded in the computer and those specified for the sample in order to ensure that the cell interior was at the real temperature T selected. This was carried out using a paraffin-filled cell

Table 3. Excess Molar Enthalpies H_m^E for Binary Systems of Ethyl Ethanoate (1) + Alkane (2) at Three Different Temperatures

x_1	H_m^E / $\mathrm{J \cdot mol^{-1}}$	x_1	H_m^E / $\mathrm{J \cdot mol^{-1}}$	x_1	H_m^E / $\mathrm{J \cdot mol^{-1}}$	x_1	H_m^E / $\mathrm{J \cdot mol^{-1}}$
$T = 291.15$ K							
Ethyl Ethanoate (1) + Pentane (2)							
0.0628	325	0.3345	1146	0.5664	1256	0.8427	733
0.1353	581	0.4047	1236	0.6434	1183	0.9116	495
0.2024	811	0.4549	1278	0.7049	1070	0.9483	272
0.2623	970	0.5140	1283	0.7712	923		
Ethyl Ethanoate (1) + Hexane (2)							
0.0535	282	0.3855	1381	0.6212	1378	0.8816	641
0.1148	581	0.4401	1440	0.6753	1294	0.9343	392
0.1974	901	0.4918	1456	0.7220	1181	0.9802	146
0.2736	1149	0.5333	1443	0.7805	1032		
0.3368	1293	0.5714	1425	0.8412	834		
Ethyl Ethanoate (1) + Heptane (2)							
0.0704	446	0.3738	1498	0.5794	1537	0.7913	1071
0.1554	830	0.4354	1568	0.6196	1485	0.8405	855
0.2363	1139	0.4887	1585	0.6682	1400	0.9015	573
0.3039	1352	0.5306	1575	0.7293	1253	0.9556	279
Ethyl Ethanoate (1) + Octane (2)							
0.0994	611	0.4740	1669	0.6953	1440	0.9435	492
0.1715	963	0.5317	1673	0.7435	1308	0.9810	243
0.2540	1266	0.5698	1641	0.7996	1139		
0.3369	1486	0.5955	1615	0.8530	944		
0.4081	1604	0.6441	1553	0.8967	737		
Ethyl Ethanoate (1) + Nonane (2)							
0.0872	551	0.4330	1689	0.6419	1645	0.8779	856
0.1735	942	0.4869	1732	0.6885	1564	0.9237	588
0.2499	1250	0.5340	1742	0.7366	1447	0.9619	307
0.3159	1468	0.5836	1724	0.7846	1298		
0.3746	1604	0.6005	1697	0.8345	1099		
Ethyl Ethanoate (1) + Decane (2)							
0.0986	609	0.4608	1764	0.6541	1710	0.8927	871
0.1909	1029	0.5067	1796	0.7009	1628	0.9375	587
0.2646	1330	0.5523	1813	0.7512	1494	0.9684	299
0.3377	1556	0.5924	1789	0.7956	1327		
0.4032	1691	0.6147	1760	0.8448	1121		
$T = 298.15$ K							
Ethyl Ethanoate (1) + Hexane (2)							
0.0668	362	0.3929	1334	0.6196	1271	0.8998	490
0.1168	572	0.4390	1375	0.6757	1195	0.9521	253
0.1920	878	0.4950	1364	0.7368	1065		
0.2621	1094	0.5309	1357	0.7954	899		
0.3186	1210	0.5767	1319	0.8424	710		
Ethyl Ethanoate (1) + Octane (2)							
0.0774	426	0.3769	1474	0.6255	1551	0.8796	801
0.1517	745	0.4335	1576	0.6736	1468	0.9202	540
0.2198	1017	0.4856	1605	0.7261	1359	0.9644	271
0.2861	1225	0.5281	1604	0.7729	1222		
0.3374	1366	0.5773	1588	0.8276	1028		
Ethyl Ethanoate (1) + Decane (2)							
0.0884	497	0.4566	1664	0.6727	1595	0.9024	776
0.1770	903	0.5101	1709	0.7191	1493	0.9385	519
0.2587	1211	0.5578	1707	0.7636	1377	0.9744	249
0.3362	1445	0.5984	1684	0.8098	1210		
0.4005	1579	0.6297	1651	0.8591	1006		
$T = 318.15$ K							
Ethyl Ethanoate (1) + Hexane (2)							
0.0760	462	0.4345	1419	0.6098	1339	0.9004	523
0.1524	815	0.4880	1415	0.6645	1259	0.9547	267
0.2306	1084	0.5143	1403	0.7202	1144		
0.3029	1256	0.5368	1393	0.7788	984		
0.3659	1360	0.5617	1384	0.8406	768		
Ethyl Ethanoate (1) + Octane (2)							
0.0832	463	0.4184	1564	0.6324	1554	0.8801	804
0.1591	814	0.4655	1607	0.6807	1485	0.9259	544
0.2322	1119	0.5112	1625	0.7307	1374	0.9646	279
0.3009	1335	0.5525	1613	0.7788	1225		
0.3637	1477	0.5886	1598	0.8291	1036		
Ethyl Ethanoate (1) + Decane (2)							
0.0892	568	0.4412	1711	0.6567	1636	0.9018	747
0.1720	947	0.4941	1756	0.6942	1566	0.9554	407
0.2474	1257	0.5409	1760	0.7429	1440		
0.3208	1480	0.5801	1743	0.7959	1268		
0.3848	1623	0.5985	1724	0.8499	1041		

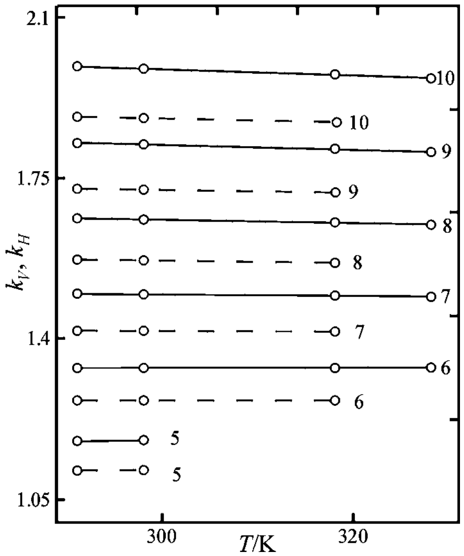

Figure 1. Variation of the parameters k_V (solid curve) and k_H (dashed curve) as functions of temperature for binary mixtures $CH_3COOC_2H_5$ (1) + C_nH_{2n+2} (2) (n = 5 to 10). Labels indicate values of n.

containing a sensor connected to an ASL F200 digital thermometer with a resolution of ± 1 mK. Similarly, before the experimental phase, the efficacy of the calorimetric block was confirmed by measuring the temperature difference between the two cells (A − B), which in no case exceeded ± 1 mK.

Electrical calibration of the apparatus was done independently at each of the three temperatures indicated above and gave excellent reproducibility for the apparatus constant. Finally, the performance of the apparatus was verified by obtaining the values of H_m^E for benzene + hexane mixtures at 298.15 K and benzene + propan-1-ol mixtures at 318.15 K and comparing the results with those recorded in the literature[25,26] for these mixtures. The uncertainty in the experimental results was estimated to be less than 1 % for H_m^E; the uncertainty of the ester composition x_1 was found to be $\pm\, 2 \cdot 10^{-4}$.

Results

Excess Properties. Presentation and Treatment of V_m^E and H_m^E. Table 2 shows the experimental (x_1, V_m^E) data obtained for all of the binary mixtures of ethyl ethanoate (1) + alkane (C_5 to C_{10}) (2) at temperatures of (291.15, 298.15, 318.15, and 328.15) K, except for the ethyl ethanoate + pentane system, for which values of V_m^E and H_m^E were measured only at (291.15 and 298.15) K, since the normal boiling temperature of pentane is $T_{b,i}^{\circ} = 309.30$ K. The (x_1, H_m^E) data measured at (291.15, 298.15, and 318.15) K are shown in Table 3. The values of the excess properties V_m^E and H_m^E were correlated as a function of the ester composition and temperature using a polynomial equation for a generic excess function Y_m^E of the form

$$Y_m^E = z_1 z_2 \sum_{i=0}^{2} a_i z_1{}^i = z_1(1 - z_1)(a_0 + a_1 z_1 + a_2 z_1{}^2) \tag{1}$$

where the coefficients a_i are expressed as functions of the temperature according to the expression

Table 4. Coefficients V_{ij} and the Standard Deviations $10^9 \cdot s(V_m^E)$ at Various Temperatures Obtained Using Equation 1 To Correlate $10^9 \cdot V_m^E/(m^3 \cdot mol^{-1}) = \varphi(x_1, T)$ for Ethyl Ethanoate (1) + Alkane (2) Mixtures

	alkane					
	pentane	hexane	heptane	octane	nonane	decane
V_{00}	$2573 \cdot 10^4$	−4901	$3951 \cdot 10^2$	$-9871 \cdot 10^2$	$4080 \cdot 10^2$	$6096 \cdot 10^2$
V_{01}	$-2545 \cdot 10^2$	−8838	−9915	−1437	−9683	−8795
V_{02}	587	52	54	44	58	55
V_{10}	$-1673 \cdot 10^4$	$9998 \cdot 10^2$	$9123 \cdot 10^2$	$9997 \cdot 10^2$	$2661 \cdot 10^2$	$9861 \cdot 10^2$
V_{11}	$3691 \cdot 10^2$	2390	344	2806	6705	236
V_{12}	−1092	−46	−42	−55	−64	−58
V_{20}	$794 \cdot 10^4$	$3266 \cdot 10^2$	$9928 \cdot 10^2$	$-4345 \cdot 10^2$	$-4975 \cdot 10^2$	$4928 \cdot 10^2$
V_{21}	$-2685 \cdot 10^2$	−3652	−8412	−1531	−990	−9920
V_{22}	839	22	33	29	31	54
k_V	1.178	1.336	1.495	1.656	1.818	1.982
$s[V_m^E(T = 291\ K)]$	18	15	8	14	10	12
$s[V_m^E(T = 298\ K)]$	23	17	18	16	13	11
$s[V_m^E(T = 318\ K)]$	−	12	16	15	15	21
$s[V_m^E(T = 328\ K)]$	−	16	11	13	16	14

Table 5. Coefficients H_{ij} and the Standard Deviations $s(H_m^E)$ at Various Temperatures Obtained Using Equation 1 To Correlate $H_m^E/(J \cdot mol^{-1}) = \varphi(x_1, T)$

	alkane					
	pentane	hexane	heptane	octane	nonane	decane
H_{00}	$6638 \cdot 10^4$	$6322 \cdot 10^4$	$4676 \cdot 10^4$	$5208 \cdot 10^4$	$2438 \cdot 10^4$	$11025 \cdot 10^4$
H_{01}	$-4526 \cdot 10^2$	$-4194 \cdot 10^2$	$-2912 \cdot 10^2$	$-3253 \cdot 10^2$	$-1431 \cdot 10^2$	$-7148 \cdot 10^2$
H_{02}	792	720	480	538	241	1195
H_{10}	$-3464 \cdot 10^4$	$-4044 \cdot 10^4$	$-5032 \cdot 10^4$	$-1270 \cdot 10^4$	$3899 \cdot 10^4$	$-5905 \cdot 10^4$
H_{11}	$3039 \cdot 10^2$	$3036 \cdot 10^2$	$3055 \cdot 10^2$	$523 \cdot 10^2$	$-2865 \cdot 10^2$	$3875 \cdot 10^2$
H_{12}	−643	−580	−483	−66	484	−681
H_{20}	$11544 \cdot 10^4$	$8837 \cdot 10^4$	$5751 \cdot 10^4$	$-6234 \cdot 10^4$	$7521 \cdot 10^4$	$-3812 \cdot 10^4$
H_{21}	$-7794 \cdot 10^2$	$-6102 \cdot 10^2$	$-3587 \cdot 10^2$	$4313 \cdot 10^2$	$-4693 \cdot 10^2$	$2507 \cdot 10^2$
H_{22}	1321	1059	566	−725	745	−385
k_H	1.114	1.265	1.417	1.570	1.724	1.879
$s[H_m^E(T = 291\ K)]$	19	11	11	32	16	13
$s[H_m^E(T = 298\ K)]$	11	13	11	30	9	10
$s[H_m^E(T = 318\ K)]$	−	8	10	6	11	13

$$a_i = \sum_{j=0}^{2} Y_{ij}T^{j-1} = \frac{Y_{i0}}{T} + Y_{i1} + Y_{i2}T \qquad (2)$$

and $z_1 = x_1/(x_1 + kx_2)$ is the *active fraction* of the ester in relation to the composition of the mixture. The parameter k was assigned a different significance depending on the property considered. For example, for the case of the excess properties studied, we used that specified in previous works[6−8] and explained briefly below. To correlate the (x_1, V_m^E) data, this parameter (represented as k_V) was determined as the ratio of the molar volumes at the measuring temperature, $V_{m,i}^{\circ}(T)$, for the compounds in the mixture. To correlate the values of (x_1, H_m^E), the parameter k (represented as k_H) was calculated as a function of $k_V(T)$ using the expression

$$k_H = \left(\frac{q_2}{q_1}\right)\left(\frac{V_{m,2}^{\circ}}{V_{m,1}^{\circ}}\right)^{2/3}\left(\frac{r_1}{r_2}\right)^{2/3} = k_q\left(\frac{k_V}{k_r}\right)^{2/3} \qquad (3)$$

where q_i and r_i ($i = 1, 2$) respectively correspond to the area and volume parameters obtained using a group contribution method from the corresponding van der Waals group parameters presented by Bondi.[27] Figure 1 shows the changes in the values of the parameters k_V and k_H with T, all of which have slopes close to zero, with the largest one ($-7 \cdot 10^{-4}$ K^{-1}) corresponding to the ethyl acetate + decane mixture.

Values of the coefficients Y_{ij} in eq 2 for V_m^E and H_m^E are shown in Tables 4 and 5, respectively. These coefficients were determined by using a least-squares procedure to minimize the standard deviation $s(Y_m^E)$ between the experimental data and the values estimated with the function. Values of s are also shown in these tables. Figure 2a gives the experimental data points and the best-fit curves for (x_1, V_m^E) at the temperatures (291.15 and 298.15) K, and its inset shows the changes in the equimolar values with n, the number of carbon atoms in the saturated hydrocarbon C_nH_{2n+2}; these data facilitate the interpretation of the behavior of these binary systems. Figure 6 compares the data for (x_1, V_m^E) obtained here with those published in the literature[9] and shows good agreement. To avoid confusion with the previous figure, Figure 2b represents the data and best-fit curves at the other two temperatures, (318.15 and 328.15) K. Similarly, Figure 3a,b shows the data and the best-fit curves for H_m^E at the three temperatures studied and the corresponding inset. Analysis of the representations in Figure 2 shows that the expansive effects of these systems increase with temperature and that $(\partial V_m^E/\partial T)_{p,x} > 0$ in all cases. However, the very different behavior of H_m^E with temperature is noteworthy, since the ratio

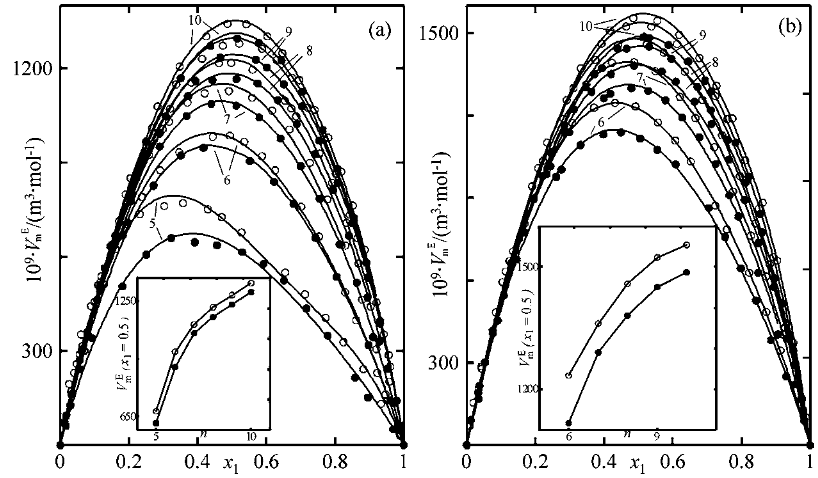

Figure 2. Experimental values of V_m^E vs x_1 and corresponding correlation curves for the binary mixtures $CH_3COOC_2H_5$ (1) + C_nH_{2n+2} (2). Labels indicate the number of carbons, n. The inset presents the variation of the equimolar volume as a function of n and temperature. (a) ●, 291.15 K; ○, 298.15 K. (b) ●, 318.15 K; ○, 328.15 K.

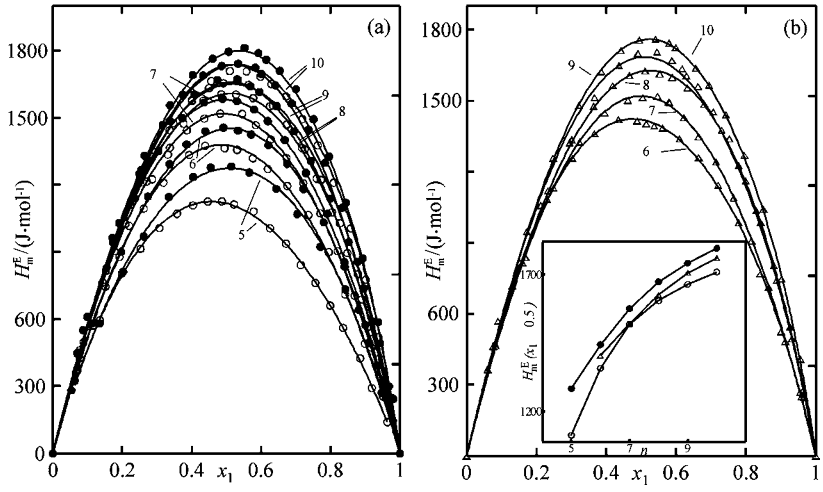

Figure 3. Experimental values H_m^E vs x_1 and corresponding correlation curves for the binary mixtures $CH_3COOC_2H_5$ (1) + C_nH_{2n+2} (2). Labels indicate the number of carbons, n. The inset presents the variation of the equimolar enthalpy as a function of n and temperature. (a) ●, 291.15 K; ○, 298.15 K. (b) ●, 291.15 K; ○, 298.15 K; △, 318.15 K.

Table 6. Experimental Vapor Pressures for Pure Ethyl Ethanoate and Alkanes

T / K	p_i° / kPa	T / K	p_i° / kPa	T / K	p_i° / kPa	T / K	p_i° / kPa	T / K	p_i° / kPa	T / K	p_i° / kPa
Ethyl Ethanoate											
297.17	11.89	327.41	44.98	343.03	79.83	351.12	104.65	357.35	127.89	365.52	163.99
303.35	16.04	329.77	49.27	344.11	82.56	351.77	106.84	357.92	130.00	366.29	167.81
306.25	18.33	331.51	52.56	345.53	86.85	352.12	108.13	358.74	133.45	367.00	171.33
308.86	20.64	333.07	55.72	346.86	90.81	352.94	111.21	359.44	136.34	367.64	174.65
310.67	22.44	335.02	59.91	348.09	94.63	353.91	114.65	360.03	139.07	367.98	176.37
312.53	24.34	336.33	62.83	348.75	96.74	354.43	116.46	360.88	142.55	368.83	180.88
315.44	27.63	337.91	66.49	349.45	98.97	354.93	118.56	361.73	146.37	369.49	184.43
318.46	31.33	339.09	69.34	349.56	99.36	355.50	120.68	362.62	150.43	370.07	187.47
321.01	34.85	340.23	72.26	349.76	100.07	355.91	122.31	363.72	155.58	370.69	190.92
323.47	38.43	341.69	76.02	349.93	100.68	356.37	124.00	364.25	157.94	371.50	195.35
324.80	40.61			350.15	101.32			364.81	160.53		
Hexane											
292.98	15.88	320.83	49.63	335.65	82.94	344.69	110.65	352.53	139.99	358.88	167.98
296.27	18.39	322.02	51.87	336.53	85.40	345.43	113.16	352.83	141.31	359.18	169.31
298.95	20.69	323.45	54.51	337.38	87.73	346.05	115.31	353.22	142.80	359.69	171.84
302.20	23.81	324.35	56.42	338.26	90.28	346.66	117.46	353.87	145.75	359.90	172.89
304.49	26.19	325.74	59.15	339.25	93.18	347.36	119.99	354.23	147.04	360.51	175.78
306.76	28.77	327.09	62.05	340.10	95.79	348.05	122.52	354.71	149.34	360.80	177.31
308.28	30.68	327.99	64.02	340.92	98.28	348.44	124.01	355.40	152.14	361.09	178.67
310.14	32.97	329.13	66.61	341.17	99.08	349.04	126.23	355.66	153.31	361.54	180.95
311.96	35.53	330.14	68.93	341.60	100.39	349.61	128.44	356.04	155.14	361.86	182.61
313.70	37.95	330.93	70.86	341.88	101.32	349.82	129.32	356.52	157.29	362.43	185.32
315.07	40.10	331.87	73.11	342.34	102.83	350.34	131.23	357.01	159.38	362.68	186.64
316.51	42.30	332.87	75.62	343.01	104.95	350.82	133.07	357.38	161.05	362.98	188.20
317.91	44.59	333.77	78.04	343.62	106.98	351.42	135.49	357.80	162.94	363.52	191.05
319.58	47.35	334.61	80.11	344.52	110.01	351.93	137.54	358.47	166.02	363.95	193.35
Heptane											
305.26	8.32	339.56	35.53	356.25	63.11	368.83	93.46	377.17	119.14	396.50	199.97
310.22	10.55	341.35	37.87	357.84	66.42	369.84	96.33	377.51	120.32		
314.93	13.09	342.96	40.12	358.68	68.27	370.85	98.98	378.49	123.70		
316.50	14.07	344.47	42.35	359.98	71.15	371.11	100.00	379.37	126.80		
319.71	16.19	346.04	44.75	361.33	74.25	371.35	100.68	380.26	130.00		
323.62	19.10	347.28	46.71	362.30	76.55	371.56	101.32	380.83	132.04		
326.44	21.45	348.72	49.09	363.32	79.00	372.42	103.92	392.89	182.39		
329.04	23.79	350.12	51.49	364.24	81.28	373.25	106.48	393.79	186.60		
331.48	26.14	351.21	53.41	365.32	84.05	373.98	108.71	394.43	189.67		
333.21	27.97	352.49	55.76	366.20	86.30	374.93	111.77	395.10	192.97		
335.50	30.51	353.62	57.88	366.87	88.10	375.41	113.35	395.73	196.04		
337.48	32.84	354.79	60.18	367.97	91.09	376.29	116.21	396.09	197.85		
Octane											
350.64	21.09	372.39	45.57	386.29	70.52	396.95	96.14	403.32	114.65	410.83	139.87
353.05	23.14	374.01	48.04	387.45	73.02	397.90	98.73	403.81	116.17	422.10	185.56
355.76	25.56	375.61	50.59	388.55	75.43	398.19	99.59	404.10	117.10	422.64	188.02
356.97	26.70	377.00	52.90	389.65	77.94	398.59	100.68	404.79	119.25	423.26	190.85
358.82	28.55	378.25	55.02	390.56	80.05	398.83	101.32	405.51	121.60	423.76	193.15
361.59	31.58	380.03	58.20	391.60	82.51	399.61	103.61	406.27	124.10	424.15	195.02
363.86	34.16	381.34	60.63	392.60	84.94	400.53	106.23	407.03	126.61	424.76	197.87
365.82	36.53	382.42	62.68	393.47	87.09	401.23	108.30	407.89	129.50	425.20	199.97
367.65	38.88	383.64	65.07	394.37	89.39	402.03	110.71	408.75	132.46		
369.09	40.82	384.76	67.34	395.14	91.38	402.81	113.09	409.62	135.53		
370.77	43.19			396.04	93.64			410.15	137.42		
Nonane											
365.30	15.58	396.96	46.56	413.68	76.48	424.92	104.00	435.58	136.62	444.23	168.53
369.25	18.07	398.71	49.15	414.83	79.03	425.83	106.50	436.31	139.12	444.93	171.39
372.81	20.58	400.61	52.12	415.90	81.41	426.71	108.99	437.11	141.90	445.49	173.63
376.46	23.49	402.01	54.42	417.22	84.44	427.60	111.54	437.95	144.81	446.19	176.52
379.71	26.35	403.31	56.55	418.24	86.85	428.40	113.88	438.67	147.42	446.75	178.85
382.25	28.78	404.73	59.01	419.28	89.41	429.26	116.44	439.45	150.23	447.44	181.82
384.65	31.22	406.27	61.77	420.50	92.43	430.22	119.35	440.11	152.67	448.07	184.55
387.02	33.80	407.78	64.58	421.62	95.25	431.09	122.04	440.76	155.08	448.61	186.86
389.45	36.62	408.93	66.76	422.83	98.40	432.04	124.99	441.41	157.53	449.27	189.75
391.80	39.52	410.11	69.09	423.20	99.35	432.94	127.82	442.05	159.98	449.81	192.13
393.48	41.74	411.32	71.53	423.61	100.44	433.74	130.52	442.77	162.80	450.56	195.54
395.26	44.15	412.52	74.01	423.94	101.32	434.68	133.60	443.49	165.61		
Decane											
386.86	15.86	420.74	48.95	438.92	81.70	450.33	109.39	460.02	138.64	469.38	172.45
390.21	17.94	422.51	51.55	440.19	84.46	451.31	112.15	460.42	140.00	470.03	175.03
393.85	20.43	424.11	54.05	441.29	86.98	452.10	114.36	461.26	142.82	470.60	177.34
397.62	23.28	425.85	56.84	442.23	89.20	452.89	116.67	462.10	145.65	471.20	179.77
400.90	26.08	427.50	59.60	443.35	91.83	453.87	119.46	463.01	148.84	471.77	182.08
403.65	28.54	429.13	62.41	444.37	94.30	454.70	121.94	463.75	151.40	472.23	184.14
406.20	31.10	430.69	65.23	444.80	95.20	455.13	123.25	464.39	153.69	472.78	186.39
408.52	33.59	432.29	68.16	446.16	98.41	455.92	125.63	465.12	156.40	473.35	188.80
411.20	36.58	433.61	70.76	446.55	99.37	456.82	128.40	465.77	158.65	474.12	191.58
413.60	39.44	435.15	73.71	446.97	100.62	457.59	130.81	466.55	161.57	474.81	194.61
414.92	41.05	436.57	76.61	447.30	101.32	458.40	133.37	467.33	164.47	475.37	197.04
416.83	43.54	437.52	78.69	448.21	103.75	459.16	135.82	468.04	167.22		
419.01	46.44			449.29	106.58			468.81	170.16		

Table 7. Coefficients *A*, *B*, and *C* of the Antoine Equation, $\log(p_i^\circ/\mathrm{kPa}) = A - B/[(T/\mathrm{K}) - C]$, and Acentric Factors ω for Pure Compounds Used in This Work To Calculate the Activity Coefficients, Along with Values from the Literature for Comparison

compound	*A*[a]	*B*[a]	*C*[a]	ω	interval of *T*/K
ethyl ethanoate	6.1440	1195.33	61.28		295 to 375
	(2.5665)	(2.2844)	(0.117)	0.353	
	6.22723[b]	1245.33[b]	55.24[b]	0.354[e]	
	6.18799[g]	1224.66[g]	57.44		270 to 375
pentane	6.02546[c]	1086.22[c]	38.76[c]	0.260[f]	309 to 323
hexane	5.9783	1154.37	51.29		290 to 365
	(2.5054)	(2.2755)	(0.101)	0.294	
	6.00266[b]	1171.53[b]	48.78[b]	0.297[d]	
	5.96291[d]	1141.62[d]	53.22[d]	0.295[e]	
heptane	5.9705	1229.82	61.37		300 to 400
	(2.5383)	(2.2768)	(0.114)	0.345	
	6.02730[b]	1268.11[b]	56.25[b]	0.346[e]	
octane	6.0066	1324.70	67.72		345 to 430
	(2.6167)	(2.3294)	(0.119)	0.393	
	6.04867[b]	1355.13[b]	63.63[b]	0.396[d]	
	6.32122[d]	1525.56[d]	45.10[d]	0.395[e]	
nonane	6.0241	1399.51	75.67		360 to 455
	(2.6642)	(2.3537)	(0.127)	0.445	
	6.06003[b]	1428.81[b]	71.53[b]	0.448[e]	
decane	6.0516	1478.91	81.72		380 to 480
	(2.7355)	(2.3948)	(0.132)	0.483	
	6.07857[b]	1501.27[b]	78.66[b]	0.482[d]	
	5.98929[d]	1431.54[d]	87.52[d]	0.485[e]	

[a] Values in parentheses are the reduced parameters *a*, *b*, and *c* in eq 4. [b] Data from ref 21. [c] Data from ref 23. [d] Data from ref 19. [e] Data from ref 30. [f] Calculated from ref 23. [g] Data from ref 28.

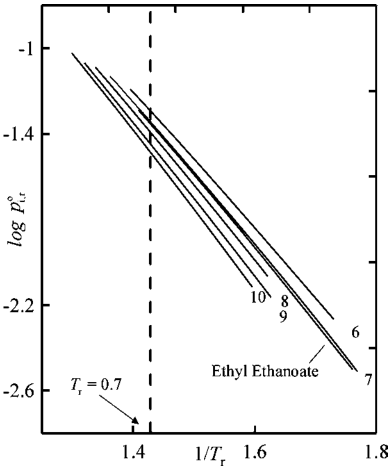

Figure 4. Vapor pressures lines in reduced coordinates for ethyl ethanoate + C_nH_{2n+2} ($n = 5$ to 10) mixtures. Labels indicate the number of carbons, *n*.

$(\partial H_m^E/\partial T)_{p,x}$ presents an inversion, changing from negative to positive with a relevant slope between the two first temperatures [from (291 to 298) K]. This anomalous behavior was also verified with other alkyl ethanoate + alkane mixtures, for which the data will be reported in the future. These data confirm the existence of this inversion and show how it diminishes as the alkanolic part of the ethanoate increases in length.

Vapor Pressures. Vapor pressure data (T, p_i°) significantly affect the determination of the thermodynamic properties of the VLE. Therefore, for this already planned series of works on alkyl ethanoates + alkanes, as mentioned in the Introduction, new data were estimated by slightly increasing the interval used in our previous works.[19] Measurements were made on all the compounds except for pentane using the same equilibrium apparatus, and the values obtained are presented in Table 6.

The (T, p_i°) pairs were correlated with the Antoine equation using a nonlinear regression procedure in MATLAB. The constants obtained are presented in Table 7 along with other values recorded in the literature for comparison. Table S1 in the Supporting Information presents a comparison between our experimental results and values from the literature[19,21,23,28] together with the mean deviations calculated for each set of data. Thus, for ethyl ethanoate, our values presented a mean error less than 0.4 % with respect to those from Ambrose et al.;[28] for the alkanes, the major difference was for decane, for which the mean error was less than 1 % in relation to the values presented by us in a previous paper.[19]

The parameter values corresponding to the Antoine equation with reduced variables in the form

$$\log p_{i,r}^\circ = a - \frac{b}{T_r - c} \tag{4}$$

were obtained directly using the regression procedure indicated previously and are shown in parentheses in Table 7. The lines ($\log p_{i,r}^\circ$) = $\varphi(1/T_r)$ are presented in Figure 4, and the vertical line corresponding to $T_r = 0.7$ is found in the temperature interval given in the last column of Table 7. Therefore, substitution of eq 4 into the Pitzer equation,[29] $\omega = -(\log p_{i,r}^\circ)_{T_r=0.7} - 1$ allowed the acentric factors ω of the pure compounds to be calculated. The values of ω obtained coincided quite well with those calculated from the constants *A*, *B*, and *C*, as described in detail in a previous work;[30] they are shown in Table 7 together with the values published by others and those estimated using the Lee−Kesler method.[31]

Presentation of VLE Data. Table 8 shows the experimental VLE (p, T, x_1, y_1) values obtained under the isobaric conditions $p = (101.32 \pm 0.02)$ *k*Pa for the six binary systems $x_1CH_3COOCH_2CH_3 + x_2C_nH_{2n+2}$ ($n = 5$ to 10). Figure 5 shows plots of $y_1 - x_1$ versus x_1 and T versus x_1,y_1 for each binary system, and Figure 6 compares the experimental data with those published in the literature for ethyl ethanoate + hexane[10] and ethyl ethanoate + octane,[11] showing an acceptable agreement among them. The activity coefficients of the liquid phase were determined by:

$$\ln \gamma_i = \ln\left(\frac{p y_i}{x_i p_i^\circ}\right) + \frac{(B_{ii} - V_{m,i}^\circ)(p - p_i^\circ)}{RT} + \frac{p}{RT}(2B_{ij} - B_{ii} - B_{jj})y_j^2 \tag{5}$$

Table 8. Experimental Data and Calculated Quantities for the Isobaric VLE of Binary Mixtures of Ethyl Ethanoate (1) + Alkane (2) at 101.32 kPa

T/K	x_1	y_1	γ_1	γ_2	G^E_m/RT	T/K	x_1	y_1	γ_1	γ_2	G^E_m/RT
Ethyl Ethanoate (1) + Pentane (2)											
309.30	0.000	0.000	−	0.986	0.000	319.40	0.617	0.233	1.125	1.448	0.214
309.70	0.036	0.023	2.791	0.991	0.029	321.73	0.686	0.276	1.095	1.553	0.201
310.05	0.068	0.040	2.579	0.995	0.060	323.88	0.736	0.314	1.067	1.647	0.179
310.58	0.107	0.061	2.451	0.999	0.095	326.83	0.782	0.368	1.051	1.687	0.153
311.13	0.150	0.079	2.217	1.011	0.129	329.55	0.828	0.423	1.030	1.814	0.127
312.20	0.246	0.106	1.736	1.069	0.186	332.28	0.867	0.483	1.017	1.945	0.103
312.50	0.267	0.113	1.683	1.081	0.196	336.05	0.904	0.570	1.007	2.034	0.074
313.19	0.314	0.127	1.562	1.112	0.213	339.51	0.936	0.658	0.995	2.228	0.046
314.22	0.381	0.147	1.423	1.166	0.229	342.42	0.960	0.740	0.989	2.517	0.026
314.85	0.430	0.158	1.323	1.225	0.236	344.50	0.978	0.804	0.993	3.228	0.019
316.21	0.492	0.179	1.239	1.285	0.233	346.70	0.988	0.875	0.994	3.655	0.009
316.80	0.515	0.190	1.224	1.305	0.233	350.15	1.000	1.000	0.994	−	0.000
317.91	0.559	0.207	1.173	1.359	0.224						
Ethyl Ethanoate (1) + Hexane (2)											
341.88	0.000	0.000	−	1.002	0.000	339.17	0.600	0.482	1.153	1.407	0.222
341.54	0.011	0.018	2.191	1.003	0.011	339.58	0.644	0.490	1.076	1.539	0.201
341.03	0.032	0.051	2.185	1.005	0.029	340.33	0.697	0.545	1.078	1.575	0.190
340.32	0.063	0.097	2.136	1.010	0.057	340.85	0.730	0.574	1.064	1.633	0.178
339.71	0.101	0.145	2.027	1.015	0.085	341.68	0.770	0.605	1.035	1.732	0.153
339.05	0.151	0.199	1.897	1.028	0.120	342.65	0.814	0.654	1.024	1.826	0.131
338.55	0.209	0.253	1.777	1.045	0.155	343.95	0.859	0.715	1.015	1.914	0.104
338.21	0.287	0.306	1.581	1.089	0.192	345.21	0.895	0.771	1.007	1.994	0.079
338.13	0.356	0.351	1.465	1.131	0.215	346.48	0.926	0.825	1.000	2.088	0.054
338.25	0.424	0.389	1.359	1.186	0.228	347.40	0.947	0.872	1.002	2.09	0.041
338.48	0.485	0.422	1.280	1.245	0.233	348.65	0.973	0.915	1.002	2.681	0.028
338.78	0.541	0.452	1.217	1.311	0.231	350.15	1.000	1.000	1.001	−	0.000
Ethyl Ethanoate (1) + Heptane (2)											
371.56	0.000	0.000	−	1.000	0.000	353.47	0.406	0.610	1.365	1.169	0.219
371.07	0.007	0.028	2.313	0.993	−0.001	352.99	0.451	0.639	1.303	1.193	0.216
370.17	0.016	0.063	2.29	0.992	0.005	352.16	0.521	0.672	1.215	1.281	0.220
369.45	0.023	0.088	2.25	0.994	0.013	351.71	0.575	0.695	1.156	1.363	0.215
368.81	0.029	0.109	2.188	0.996	0.019	351.25	0.632	0.722	1.108	1.458	0.204
367.45	0.044	0.152	2.134	1.003	0.036	350.76	0.668	0.747	1.099	1.503	0.198
366.11	0.061	0.198	2.061	1.006	0.050	350.38	0.733	0.772	1.048	1.701	0.176
365.30	0.072	0.224	2.033	1.010	0.060	350.15	0.783	0.809	1.022	1.865	0.152
364.45	0.084	0.255	2.016	1.009	0.067	349.98	0.822	0.825	1.006	2.037	0.133
362.40	0.116	0.324	1.961	1.013	0.090	349.99	0.861	0.855	0.991	2.214	0.103
360.90	0.144	0.369	1.881	1.023	0.110	350.01	0.904	0.881	0.979	2.530	0.070
359.48	0.173	0.410	1.809	1.037	0.13	350.05	0.936	0.915	0.980	2.732	0.045
357.47	0.223	0.475	1.721	1.051	0.160	350.10	0.962	0.945	0.983	2.990	0.025
355.95	0.272	0.526	1.632	1.065	0.179	350.12	0.977	0.966	0.988	3.064	0.014
354.83	0.319	0.563	1.539	1.091	0.197	350.15	1.000	1.000	1.000	−	0.000
353.95	0.357	0.593	1.483	1.112	0.209						
Ethyl Ethanoate (1) + Octane (2)											
398.83	0.000	0.000	−	1.000	0.000	360.68	0.462	0.808	1.272	1.126	0.175
395.85	0.015	0.094	1.885	0.995	0.004	359.34	0.519	0.811	1.206	1.184	0.178
392.41	0.033	0.198	1.936	0.985	0.007	357.54	0.602	0.837	1.128	1.311	0.180
387.83	0.059	0.315	1.888	0.983	0.022	356.38	0.666	0.854	1.082	1.405	0.166
385.17	0.077	0.376	1.858	0.985	0.034	354.98	0.739	0.876	1.042	1.567	0.148
382.11	0.101	0.445	1.824	0.982	0.044	353.68	0.788	0.898	1.033	1.752	0.145
380.00	0.118	0.490	1.790	0.981	0.052	352.80	0.845	0.921	1.009	1.995	0.115
377.52	0.141	0.537	1.755	0.984	0.065	352.08	0.881	0.936	1.005	2.122	0.094
374.42	0.172	0.594	1.722	0.985	0.081	351.55	0.906	0.949	1.008	2.135	0.079
371.76	0.204	0.641	1.680	0.986	0.095	351.06	0.933	0.964	1.004	2.340	0.060
367.92	0.259	0.702	1.610	0.994	0.119	350.69	0.958	0.976	1.003	2.348	0.039
365.92	0.299	0.731	1.533	1.013	0.137	350.23	0.991	0.995	1.001	2.443	0.009
363.34	0.362	0.770	1.433	1.039	0.155	350.15	1.000	1.000	1.000	−	0.000
362.37	0.400	0.785	1.360	1.067	0.162						
Ethyl Ethanoate (1) + Nonane (2)											
423.94	0.000	0.000	−	1.000	0.000	369.47	0.338	0.864	1.455	1.065	0.168
420.00	0.010	0.118	2.058	0.985	−0.008	367.15	0.412	0.879	1.292	1.167	0.196
417.06	0.017	0.189	2.125	0.985	−0.002	363.75	0.486	0.900	1.233	1.252	0.217
412.10	0.031	0.303	2.048	0.980	0.003	361.50	0.564	0.915	1.151	1.372	0.217
407.91	0.045	0.390	1.998	0.976	0.008	359.01	0.635	0.930	1.119	1.487	0.216
405.01	0.055	0.444	1.963	0.976	0.014	357.15	0.712	0.942	1.067	1.676	0.195
400.40	0.073	0.523	1.926	0.975	0.024	355.50	0.792	0.953	1.020	2.013	0.161
396.55	0.093	0.583	1.828	0.978	0.036	354.15	0.854	0.965	0.998	2.239	0.116
391.49	0.120	0.652	1.782	0.980	0.052	353.00	0.897	0.974	0.994	2.454	0.087
385.31	0.159	0.726	1.729	0.984	0.073	351.92	0.940	0.985	0.991	2.552	0.048
381.80	0.187	0.762	1.680	0.991	0.090	351.19	0.964	0.991	0.995	2.632	0.030
377.45	0.227	0.804	1.629	0.997	0.108	350.70	0.981	0.995	0.997	2.763	0.016
374.65	0.261	0.826	1.567	1.019	0.131	350.15	1.000	1.000	1.000	−	0.000

Table 8. Continued

T/K	x_1	y_1	γ_1	γ_2	G^E_m/RT	T/K	x_1	y_1	γ_1	γ_2	G^E_m/RT
					Ethyl Ethanoate (1) + Decane (2)						
487.30	0.000	0.000	–	1.000	0.000	357.59	0.682	0.973	1.136	1.572	0.231
433.02	0.026	0.320	1.747	0.997	0.012	356.21	0.764	0.978	1.062	1.833	0.189
422.86	0.047	0.501	1.813	0.985	0.022	354.55	0.819	0.983	1.047	1.987	0.162
412.23	0.073	0.643	1.838	0.987	0.033	353.76	0.859	0.986	1.026	2.176	0.132
397.98	0.118	0.782	1.867	0.992	0.067	352.95	0.888	0.989	1.020	2.232	0.107
383.62	0.186	0.876	1.855	1.004	0.118	351.75	0.925	0.993	1.021	2.240	0.080
373.72	0.258	0.921	1.810	1.017	0.166	351.40	0.951	0.995	1.006	2.488	0.050
370.71	0.296	0.933	1.731	1.023	0.178	350.46	0.980	0.998	1.008	2.545	0.026
365.23	0.393	0.951	1.546	1.082	0.219	350.37	0.990	0.999	1.002	2.556	0.011
360.76	0.529	0.964	1.322	1.235	0.247	350.15	1.000	1.000	1.000	–	0.000
359.00	0.605	0.969	1.223	1.367	0.245						

which assumes that the vapor phase is nondeal. The second virial coefficients for the pure compounds, B_{ii} and B_{jj}, and those for the mixtures, B_{ij}, were calculated using the Tsonopoulos method.[32] The molar volumes $V^\circ_{m,i}$ of the pure compounds at the equilibrium temperature were estimated from the Rackett equation as modified by Spencer and Danner[33] using the values of Z_{RA} summarized in Reid at al.[34] The vapor pressures p°_i were calculated by applying the Antoine equation using the constants given in Table 7. The calculated values of the Gibbs function $G^E_m/RT = \sum_i x_i \ln \gamma_i$ are reported in Table 8 and Figure 7a–f together with the values of the activity coefficients γ_i for each binary system. These show that the systems exhibit important deviations from ideal behavior, with an increase in the repulsive forces between the molecules of the mixture.

The six systems studied satisfy the global condition proposed by Fredenslund,[35] $\bar{\delta} = \sum_i (y_{i,\text{exptl}} - y_{i,\text{calcd}})/N \le 0.01$, and are therefore considered to be thermodynamically consistent. Mixtures of ethyl ethanoate with hexane and with heptane present an azeotrope having the coordinates given in Table 9, where they are compared with those recorded in the literature[36] for these systems.

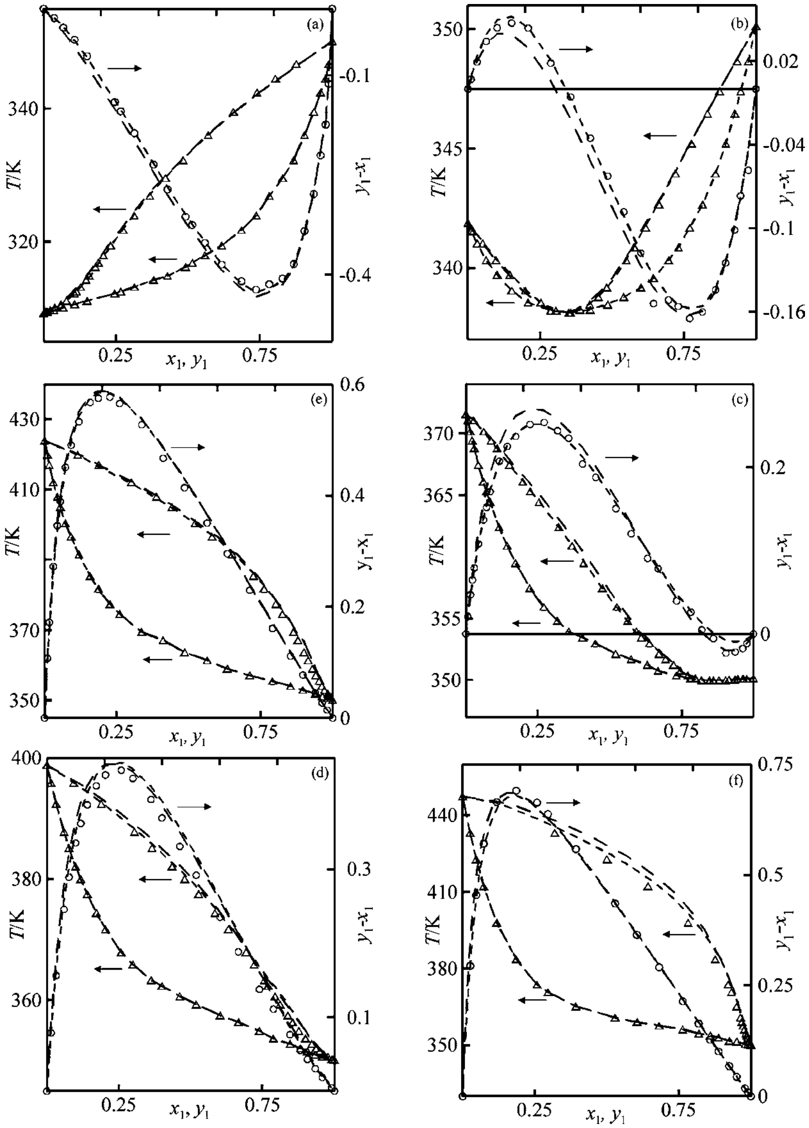

Figure 5. Plots of experimental VLE values for the binary mixtures $CH_3COOC_2H_5$ (1) + C_nH_{2n+2} (2) for n = (a) 5, (b) 6, (c) 7, (d) 8, (e) 9, and (f) 10: ○, $y_1 - x_1$ vs x_1; △, T vs x_1,y_1. Dashed lines represent the curves estimated using two versions of the UNIFAC model: (— —), ref 17; (- - -), ref 18.

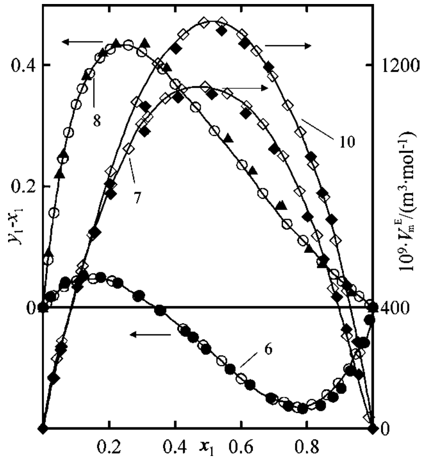

Figure 6. Comparison between our data (VLE and V_m^E) and those from the literature for the binary mixtures $CH_3COOC_2H_5$ (1) + C_nH_{2n+2} (2). VLE, $n = 6$: ○, this work; ●, ref 10. VLE, $n = 8$: ○, this work; ▲, ref 11. V_m^E, $n = 7$, 10: ◇, this work; ◆, ref 9.

Table 9. Experimental Azeotropic Coordinates (x_{1az}, T_{1az}) at p = 101.32 kPa for Binary Mixtures of Ethyl Ethanoate (1) + Alkane (2) and Comparison with Literature Values and Those Predicted Using Two Versions of the UNIFAC Model

	$x_{1,az}$, T_{az}/K	
mixture	exptl	lit
ethyl ethanoate (1) + hexane (2)	0.339, 338.15	0.343, 338.3[a] 0.318, 338.2[b] 0.339, 338.1[c]
ethyl ethanoate (1) + heptane (2)	0.834, 349.99	0.822, 350.0[b] 0.865, 350.0[c]

[a] Data from ref 36. [b] Estimated using UNIFAC.[17] [c] Estimated using UNIFAC.[18]

Treatment of VLE Data and Prediction. The values of the excess Gibbs function $G_m^E = G_m^E(x_1, T)$ obtained for the isobaric equilibria were correlated using eq 1 adapted to this function as follows:

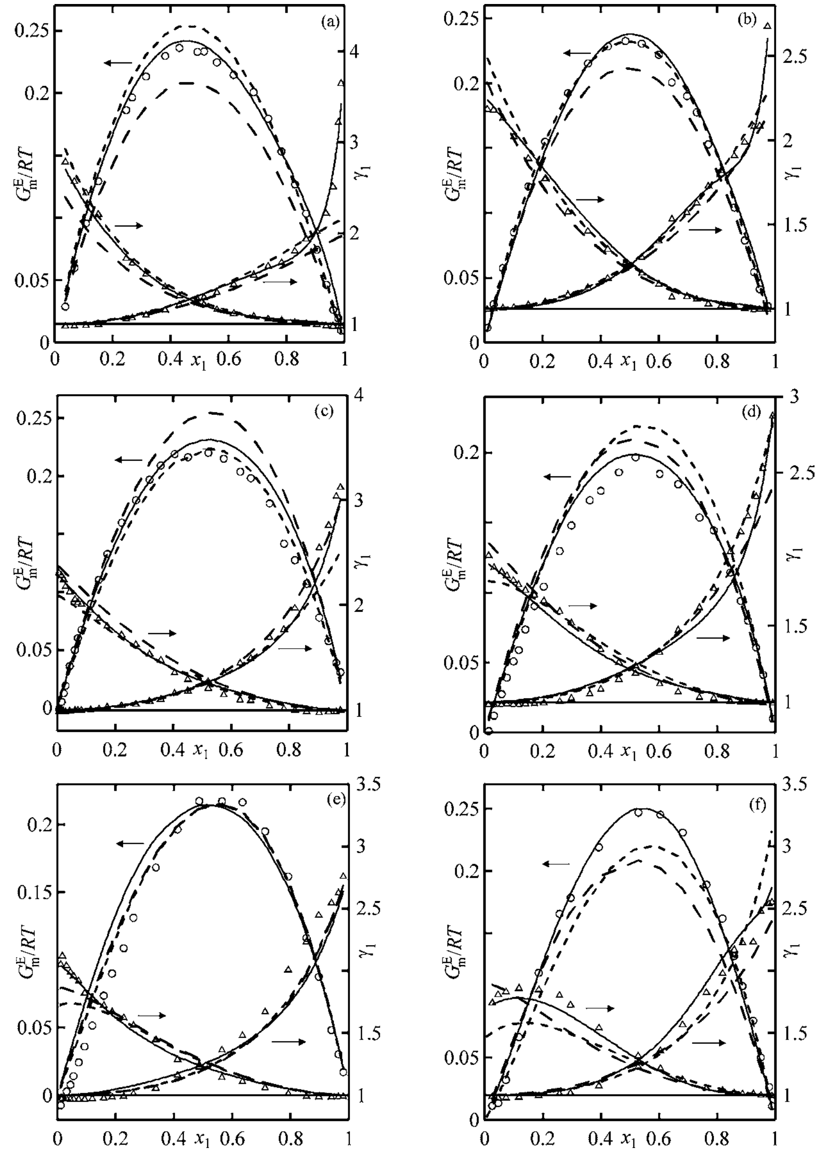

Figure 7. Comparison between experimental values (symbols) and correlated curves (solid lines) for the binary mixtures $CH_3COOC_2H_5$ (1) + C_nH_{2n+2} (2) for n = (a) 5, (b) 6, (c) 7, (d) 8, (e) 9, and (f) 10 as functions of x_1: ○, G_m^E/RT; △, γ_1. Dashed lines are the estimations obtained using two versions of the UNIFAC model: (— —), ref 17; (- - -), ref 18.

Table 10. Activity Coefficients at Infinite Dilution Obtained from VLE Data of Binary Mixtures Ethyl Ethanoate (1) + Alkane (2) Using Equations 10 and 11

	alkane					
	pentane	hexane	heptane	octane	nonane	decane
γ_1^∞	2.93	2.26	2.29	1.94	2.06	1.75
	2.61[a]	2.39[a]	2.38[a]	2.07[a]	1.87[a]	1.90[a]
	3.25[b]	2.53[b]	2.10[b]	1.79[b]	1.72[b]	1.45[b]
γ_2^∞	2.91	3.46	3.19	3.04	2.81	2.74
	1.99[a]	2.23[a]	3.18[a]	2.45[a]	2.84[a]	2.45[a]
	2.16[b]	2.37[b]	2.64[b]	2.90[b]	2.84[b]	3.25[b]

[a] Estimated using UNIFAC.[17] [b] Estimated using UNIFAC.[18]

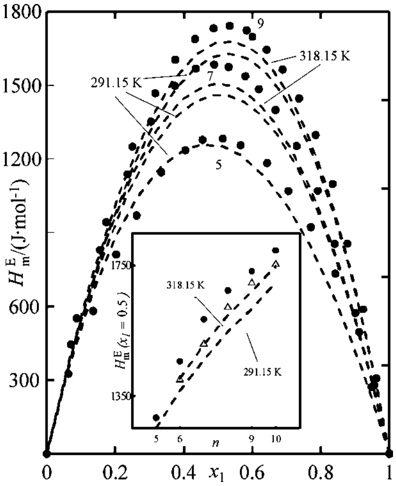

Figure 8. Comparison between experimental H_m^E values (○) at 291.15 K and the estimated curves (- - -) obtained using UNIFAC[18] at (291.15 and 318.15) K for the binary mixtures $CH_3COOC_2H_5$ (1) + C_nH_{2n+2} (2). Labels indicate *n*. The inset presents a comparison of the experimental equimolar H_m^E values (○, 291.15 K; △, 318.15 K) and the corresponding values obtained using UNIFAC.[18]

$$G_m^E(x_1, T) = z_1(1 - z_1)\sum_{i=0}^{2} g_i z_1{}^i \qquad (6)$$

where z_1 has the same significance as described above. The temperature dependence of the coefficients g_i in eq 6 was represented by the following relation:

$$g_i = \sum_{j=0}^{2} G_{ij}T^{j-1} = \frac{G_{i0}}{T} + G_{i1} + G_{i2}T \qquad (7)$$

In some cases, the number of coefficients G_{ij} in eq 7 can be reduced to avoid an overparametrization.

Classical thermodynamics allows the development of the following relation:

$$-S_m^E = \left[\frac{\partial G_m^E}{\partial T}\right]_{p,x} = z_1(1 - z_1)\sum_{i=0}^{2}\left(\frac{dg_i}{dT}\right)z_1{}^i + \left(\frac{dz_1}{dk_G}\right)\left(\frac{dk_G}{dT}\right) \times \left[(1 - 2z_1)\sum_{i=0}^{2} g_i z_1{}^i + z_1(1 - z_1)(g_1 + 2g_2 z_1)\right] \qquad (8)$$

For the practical application of this equation, we assumed that the variation of the parameter k_G with temperature was negligible, as shown for k_V and k_H in Figure 1. Therefore, eq 8 could be simplified by eliminating the second term on the right-hand side.

The excess enthalpy is related to the excess entropy and excess Gibbs energy by the expression

$$H_m^E = G_m^E + TS_m^E \qquad (9)$$

Combining eqs 6 and 8 and taking into account the definition of the coefficients g_i in eq 7 allows the enthalpy to be expressed as

$$H_m^E = z_1(1 - z_1)\left[\sum_{i=0}^{2}\left(\frac{2G_{i0}}{T} + G_{i1}\right)\right] \qquad (10)$$

The activity coefficient of each generic compound was obtained from the expression

$$\ln \gamma_i = \left(\frac{G_m^E}{RT}\right) + (1 - x_i)\left[\frac{\partial(G_m^E/RT)}{\partial x_i}\right]_{p,T} = \left(\frac{G_m^E}{RT}\right) + (1 - x_i)\left[\frac{\partial(G_m^E/RT)}{\partial z_1}\right]_{p,T}\left(\frac{dz_1}{dx_i}\right) \qquad (11)$$

Taking eq 6 and the definition of z_1 into account allows this to be written as follows:

Table 11. Parameters for Equations 5 and 9 Obtained from the Simultaneous Correlation of VLE Data and Excess Enthalpies for Ethyl Ethanoate (1) + Alkane (2) Mixtures Along with Standard Deviations $s(Y_m^E)$ for Each of the Properties ln γ_i, G_m^E/RT, and $H_m^E/J\cdot mol^{-1}$

	alkane					
	pentane	hexane	heptane	octane	nonane	decane
k_G	1.644	2.299	1.317	1.599	1.009	2.377
G_{00}	$2530\cdot10^3$	$-432\cdot10^3$	$795\cdot10^3$	$753\cdot10^3$	$1270\cdot10^3$	$1210\cdot10^3$
G_{01}	−11249	10426	3523	3685	391	3287
G_{02}	24.6	−11.2	−6.1	−5.3	−1.9	−3.0
G_{10}	$-2525\cdot10^3$	$-27\cdot10^3$	$-1259\cdot10^3$	$-926\cdot10^3$	$-257\cdot10^3$	$-2002\cdot10^3$
G_{11}	13978	−4912	1253	1015	−987	494
G_{12}	−38.7	−11.0	−1.3	−8.4	−1.2	−7.4
G_{20}	$12109\cdot10^3$	$2336\cdot10^3$	$658\cdot10^3$	$427\cdot10^3$	$-1806\cdot10^3$	$2413\cdot10^3$
G_{21}	−80541	−13249	−1474	−1550	8989	−9077
G_{22}	144.5	33.5	4.1	8.4	−5.9	15.7
$s(\ln \gamma_1)$	0.020	0.020	0.027	0.041	0.022	0.035
$s(\ln \gamma_2)$	0.029	0.022	0.039	0.090	0.067	0.035
$s(G_m^E/RT)$	0.009	0.008	0.012	0.011	0.021	0.007
$s[H_m^E(T = 291\ K)]$	23	27	21	66	81	17
$s[H_m^E(T = 298\ K)]$	15	43	26	33	83	48
$s[H_m^E(T = 318\ K)]$	−	33	13	43	66	67

$$RT \ln \gamma_i = z_i(1 - z_i)\sum_{j=0}^{2} g_j z_i^j + (1 - x_i)\left[\sum_{j=0}^{3} (j + 1)(g_j - g_{j-1})z_i^j\right]k\left(\frac{z_i}{x_i}\right)^2 \quad (12)$$

with $g_{-1} = g_3 = 0$. At infinite dilution, the activity coefficients for the two compounds in the binary system are given by

$$\ln \gamma_1^{\infty} = \lim_{x_1 \to 0} \ln \gamma_1 \equiv \lim_{z_1 \to 0} \ln \gamma_1 = \frac{g_0}{k_G R T_{b,2}^{\circ}} \quad (13)$$

$$\ln \gamma_2^{\infty} = \lim_{x_2 \to 0} \ln \gamma_2 \equiv \lim_{z_1 \to 1} \ln \gamma_2 = \frac{k_G(g_0 + g_1 + g_2)}{R T_{b,1}^{\circ}} \quad (14)$$

Table 10 shows the values of γ_i^{∞} for the mixtures studied along with the values estimated from the UNIFAC model using the group contributions given in the literature.[17,18]

Equations 6, 10 and 12 were used to carry out a simultaneous correlation of the VLE data and the excess enthalpies H_m^E using the regression procedure for nonlinear functions mentioned previously. An objective function (OF) was defined to minimize the differences between experimental values and those estimated by the model. To make the degrees of significance of the different variables equivalent, a correction coefficient c_i was introduced for each of the quantities in the OF, which finally had the following form:

$$\mathrm{OF} = c_0 s(G_m^E) + c_1 s(\ln \gamma_1) + c_2 s(\ln \gamma_2) + c_3 s(H_m^E) \quad (15)$$

where $s(E)$ is the standard deviation of the indicated variable E, defined as

$$s(E) = \left[\sum_{i=1}^{n} \frac{(E_{i,\mathrm{exptl}} - E_{i,\mathrm{calcd}})^2}{n - 1}\right]^{1/2} \quad (16)$$

Figure 7 shows the corresponding representations, and the goodness of fit for each of the statistical parameters is shown in Table 11. A stepwise correlation $(x_1, H_m^E) \to (x_1, G_m^E) \to (x_1, S_m^E)$ was also applied and gave very similar results.

Prediction of VLE. Two versions of the UNIFAC group contribution model were applied: the original version proposed by Fredenslund et al.[35] using the more recent set of parameters proposed by Hansen et al.[17] and the version of Gmehling et al.,[18] which in addition to estimating the activity coefficients γ_i also estimates the excess enthalpies H_m^E with the same set of interaction parameters. Figure 7a−f reports the results obtained with the two versions for the mixtures studied and compares them with the experimental values. The method also permitted the original equilibrium values (p, T, x_1, y_1) to be estimated; the results are presented in Figure 5a−f together with the experimental data. The two methods gave similar predictions, so the VLE data obtained are considered to be acceptable. The version of Gmehling et al.[18] gave good estimates of the H_m^E values of the mixtures, as shown in Figure 8, although it was not good at accounting for changes in temperature.

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This paper is dedicated to the memory of our good friend and colleague, Dr. Henry Kehiaian, who passed away a short time ago. Henry was an authority in many aspects of vapor−liquid equilibrium and excess properties, and on many occasions he reviewed our work professionally and in depth and offered many constructive suggestions to improve its value.

Supporting Information Available:

Table S1 comparing our experimental vapor pressures with values from the literature. This material is available free of charge via the Internet at http://pubs.acs.org.

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