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Isobaric Vapor−Liquid Equilibrium Data and Excess Properties of Binary Systems Comprised of Alkyl Methanoates + Hexane

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In this work, we report the experimental values of the excess quantities H_m^E and V_m^E and the isobaric equilibrium data (VLE) at 101.32 kPa for the four mixtures of alkyl methanoates (methyl to butyl) and hexane. The results indicate that for these four mixtures $(\partial H_m^E/\partial T)_p > 0$ and$(\partial V_m^E/\partial T)_p > 0$. VLE data were found to be thermodynamically consistent with the Fredenslund method. All the binary mixtures presented here, except for the system (butyl methanoate + hexane), present a minimum-boiling temperature azeotrope with coordinates (x_{az}, T_{az}/K), (0.832, 302.62) for (methyl methanoate + hexane), (0.703, 323.32) for (ethyl methanoate + hexane), and (0.283, 339.10) for (propyl methanoate + hexane). Simultaneous correlations performed with the VLE data and excess enthalpies using a simple polynomial model, with temperature-dependent coefficients, produced acceptable estimations. Application of the UNIFAC model in the versions of Hansen et al. (*Ind. Eng. Chem. Res*. **1991**, *30*, 2355−2358) and Gmehling et al. (*Ind. Eng. Chem. Res*. **1993**, *32*,178−193) produced similar predictions for all four systems, of which only the ones for the methyl methanoate + hexane mixture are acceptable. Differences increase steadily with increasing methanoate chain length. Estimation of enthalpies with the second of the versions indicated, however, produced mean errors of 10 %, which could be considered as acceptable.

Introduction

For several years, our research group has been studying the thermodynamic properties of mixtures containing alkyl esters. In the field of vapor−liquid equilibria (VLE), a considerable amount of work has been conducted on binary systems of esters + alkanols, providing an important experimental contribution to these systems and specifically to mixtures containing alkyl methanoates.[1−7] However, when working with theoretical modeling based on group contribution methods, the predictions were found to be unacceptable, revealing in some cases large discrepancies. A literature review shows only few studies of VLE of mixtures of alkyl methanoates + alkanes mixtures.[1,3,4,8] These binary systems are considered as a preliminary work since they have helped to establish the behavior of methanoates in solution with inert substances such as alkanes as well as providing interesting information about the CH_2/HCOO interaction. We have published data on the excess enthalpies H_m^E and volumes V_m^E at 298.15 K for binary systems composed of (alkyl methanoates + alkanes),[3,4,9−12] which will also be used in this study. Also, VLE data of the binary system (ethyl methanoate + hexane) were measured at 101.32 kPa and published in a previous paper.[3] VLE data[8] at 101.32 kPa and LLE[13] at 19 kPa have been reported for the system (methyl methanoate + hexane) along with values of H_m^E at T = 298.15 K for the system (ethyl methanoate +hexane).[14]

In this first work of the series in which hexane is the common substance, a series of studies will be carried out systematically on mixtures of alkyl methanoates (methyl to butyl) with different alkanes. In this way, we will help to expand the existing database, obtaining more information about the behavior of these substances. Moreover, modeling of primary systems (methanoates + alkanes) will help us to define the CH_2/HCOO interaction, which will improve predictions of other systems that involve the G/HCOO interaction of methanoates with another functional group G. In this sense, this project on methanoates will include extensive experimental information with data of VLE, H_m^E, and V_m^E measured at different temperatures. Since data for H_m^E and V_m^E at 298.15 K have already been presented in previous works,[1−14] we decided to provide experimental data for these excess properties at other temperatures.

Another important aspect of this series of works is to verify the suitability of a new procedure to treat VLE data and to study the predictive capacity of the UNIFAC group contribution method using the original version with the parameters of Hansen et al.[15] and the newer version of Gmehling et al.,[16] which can be used to estimate properties different from VLE using the same set of interaction parameters.

Experimental Section

Materials. Alkyl methanoates and alkanes used in the experimental part of this work are of the highest commercial purity and were supplied by Aldrich. Nonetheless, before their use, all the products were subjected to a preliminary treatment that consisted of degassifying by ultrasound for a sufficient length of time, followed by moisture reduction using a 0.3 nm Fluka molecular sieve. The quality of the products was verified with a GC model HP6890 and found to be similar to that indicated by the manufacturer. The purity of the products used

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Table 1. Physical Properties of Pure Compounds

		$T^\circ_{b,i}$		T	$\rho/kg{\cdot}m^{-3}$		$10^3\ \bar{\alpha}/K^{-1}$		n_D		$10^4\ b$	
compound	mass fraction	exp	lit	K	exp	lit	exp	lit	exp	lit	exp	lit
$HCOOCH_3$	>0.99	304.70	304.90[a] 304.79[b]	291.15→	976.90	977.25[c]	1.46	1.56[g]	1.3452			
				298.15→	966.54	966.40[a] 966.18[b]			1.3415	1.3415[a] 1.3412[b]	5	4[a]
$HCOOCH_2CH_3$	>0.97	327.33	327.46[a]	291.15→	924.70	924.59[c]			1.3614		5	5[a]
				298.15→	915.16	915.30[a]	1.48	1.42[g]	1.3580	1.3575[a]		
				318.15→	888.42	888.19[d]			1.3474	1.3475[d]		
$HCOO(CH_2)_2CH_3$	>0.97	353.92	353.97[a]	291.15→	907.80	907.70[c]			1.3778		5	5[a]
				298.15→	899.08	899.60[a]	1.33	1.28[g]	1.3750	1.3750[a]		
				318.15→	875.32	875.56[e]			1.3650	1.3650[e]		
$HCOO(CH_2)_3CH_3$	>0.97	380.13	379.25[a]	291.15→	896.00	893.75[c]			1.3904			
				298.15→	888.66	886.90[a]	1.21		1.3872	1.3874[a]	5	4[a]
				318.15→	867.21	867.74[f]			1.3776	1.3773[f]		
$CH_3(CH_2)_4CH_3$	>0.99	341.76	341.89[a]	291.15→	661.20	660.92[c]			1.3765			
				298.15→	654.89	654.84[a]	1.41	1.39[g]	1.3720	1.3722[a]	5	5[a]
				318.15→	636.43	636.39[d]			1.3618	1.3614[d]		

[a] Ref 17. [b] Ref 4. [c] Values interpolated from ref 19. [d] Ref 3. [e] Ref 7. [f] Ref 6. [g] Ref 18. $\bar{\alpha}$, average expansion coefficient; b, slope of $n_D = a + bT$.

Table 2. Densities ρ and Excess Molar Volumes V_m^E for Binary Systems of Alkyl Methanoate (1) + Hexane (2) at Three Different Temperatures

	ρ	$10^9\ V_m^E$		ρ	$10^9\ V_m^E$		ρ	$10^9\ V_m^E$		ρ	$10^9\ V_m^E$		ρ	$10^9\ V_m^E$
x_1	$kg{\cdot}m^{-3}$	$m^3{\cdot}mol^{-1}$	x_1	$kg{\cdot}m^{-3}$	$m^3{\cdot}mol^{-1}$	x_1	$kg{\cdot}m^{-3}$	$m^3{\cdot}mol^{-1}$	x_1	$kg{\cdot}m^{-3}$	$m^3{\cdot}mol^{-1}$	x_1	$kg{\cdot}m^{-3}$	$m^3{\cdot}mol^{-1}$
$T = 291.15$ K														
Methyl Methanoate (1) + Hexane (2)														
0.0000	661.20	0	0.1013	672.60	804	0.3828	718.90	1885	0.6987	810.10	1435	0.9030	908.40	501
0.0190	663.00	200	0.1209	675.30	894	0.4841	742.30	1926	0.7445	829.10	1212	0.9539	939.90	267
0.0499	666.30	470	0.2033	687.10	1301	0.5462	759.10	1857	0.7956	851.50	1034	1.0000	976.90	0
0.0863	670.60	730	0.2986	702.60	1700	0.6061	777.40	1725	0.8392	872.60	861			
Ethyl Methanoate (1) + Hexane (2)														
0.0000	661.20	0	0.2049	692.10	890	0.5016	753.0	1244	0.8029	842.40	757	0.9522	901.90	267
0.0495	667.80	300	0.2531	700.40	1044	0.6039	780.00	1114	0.8259	860.90	616	0.9580	905.00	197
0.1025	675.40	571	0.3068	710.60	1124	0.6996	808.20	956	0.9016	880.30	450	1.0000	924.70	0
0.1497	682.80	744	0.3937	728.20	1241	0.7504	824.60	851	0.9065	882.40	425			
Propyl Methanoate (1) + Hexane (2)														
0.0000	661.20	0	0.2001	696.50	610	0.5017	761.80	756	0.8013	842.80	417	1.0000	907.80	0
0.0544	670.10	237	0.2480	705.80	694	0.6122	789.60	676	0.8499	857.80	326			
0.0893	676.00	374	0.2521	706.60	703	0.6985	813.10	556	0.9057	875.50	234			
0.1509	687.40	477	0.3979	737.60	782	0.7473	827.00	483	0.9568	892.90	88			
Butyl Methanoate (1) + Hexane (2)														
0.0000	661.20	0	0.1928	699.50	414	0.5021	768.30	466	0.8020	842.70	226	1.0000	896.00	0
0.0445	669.60	152	0.2490	711.40	459	0.5957	790.70	412	0.8532	856.10	179			
0.0900	678.60	247	0.3018	722.70	504	0.6963	815.70	318	0.8987	868.20	132			
0.1461	689.80	364	0.4025	745.20	505	0.7541	830.40	262	0.9575	884.30	46			
$T = 298.15$ K														
Methyl Methanoate (1) + Hexane (2)														
0.0000	654.89	0	0.1642	674.80	1156	0.4987	740.05	1886	0.7972	845.31	1089	1.0000	966.54	0
0.0376	659.63	165	0.2352	685.32	1519	0.5979	768.90	1700	0.8497	871.94	805			
0.0816	664.26	591	0.2936	695.29	1708	0.7062	806.50	1436	0.9050	902.05	595			
0.1327	670.55	964	0.3903	714.41	1867	0.7433	821.74	1278	0.9582	936.28	273			
Ethyl Methanoate (1) + Hexane (2)														
0.0000	654.89	0	0.1715	679.95	776	0.4765	739.84	1214	0.6441	783.83	1012	0.8840	865.42	373
0.0777	665.63	394	0.2501	693.44	976	0.5354	754.13	1192	0.6993	800.39	904	0.9643	898.98	104
0.1291	673.25	622	0.3270	707.73	1135	0.5955	769.95	1118	0.7956	832.38	647	1.0000	915.16	
0Propyl Methanoate (1) + Hexane (2)														
0.0000	654.89	0	0.2941	709.36	705	0.5453	765.36	783	0.7650	824.15	509	0.9567	884.05	123
0.0787	668.91	284	0.3597	722.93	778	0.6019	779.74	713	0.8120	838.34	385	1.0000	899.08	0
0.1478	681.52	399	0.4297	738.37	784	0.6599	794.74	675	0.8656	854.66	297			
0.2237	695.63	573	0.4878	751.68	789	0.7154	810.00	590	0.9210	872.18	206			
Butyl Methanoate (1) + Hexane (2)														
0.0000	654.89	0	0.2658	708.76	391	0.5876	781.81	361	0.8574	849.77	113	1.0000	888.66	0
0.0729	669.39	106	0.3360	723.94	423	0.6855	805.81	277	0.8986	860.63	76			
0.1321	681.03	243	0.3698	731.40	429	0.7677	826.55	200	0.9227	867.09	47			
0.1967	694.20	335	0.4886	758.31	428	0.8136	838.26	167	0.9714	880.08	18			
$T = 308.15$ K														
Ethyl Methanoate (1) + Hexane (2)														
0.0000	646.07	0	0.1539	667.20	810	0.4915	731.90	1395	0.7971	819.90	810	1.0000	902.07	0
0.0485	651.90	320	0.2548	683.80	1137	0.5935	757.80	1255	0.9063	860.70	458			
0.1103	660.50	654	0.3998	711.60	1372	0.6998	788.00	1086	0.9488	878.70	264			

Table 2 (Continued)

x_1	ρ / $\mathrm{kg{\cdot}m^{-3}}$	$10^9\,V_{\mathrm{m}}^{\mathrm{E}}$ / $\mathrm{m^3{\cdot}mol^{-1}}$	x_1	ρ / $\mathrm{kg{\cdot}m^{-3}}$	$10^9\,V_{\mathrm{m}}^{\mathrm{E}}$ / $\mathrm{m^3{\cdot}mol^{-1}}$	x_1	ρ / $\mathrm{kg{\cdot}m^{-3}}$	$10^9\,V_{\mathrm{m}}^{\mathrm{E}}$ / $\mathrm{m^3{\cdot}mol^{-1}}$	x_1	ρ / $\mathrm{kg{\cdot}m^{-3}}$	$10^9\,V_{\mathrm{m}}^{\mathrm{E}}$ / $\mathrm{m^3{\cdot}mol^{-1}}$	x_1	ρ / $\mathrm{kg{\cdot}m^{-3}}$	$10^9\,V_{\mathrm{m}}^{\mathrm{E}}$ / $\mathrm{m^3{\cdot}mol^{-1}}$
$T = 308.15$ K														
Propyl Methanoate (1) + Hexane (2)														
0.0000	646.07	0	0.1993	680.76	585	0.5069	745.56	848	0.8034	824.55	484	1.0000	888.36	0
0.0693	657.50	254	0.3036	701.12	747	0.5902	765.82	817	0.9002	854.72	260			
0.1125	665.10	358	0.3975	720.81	827	0.7035	795.66	687	0.9482	870.44	149			
Butyl Methanoate (1) + Hexane (2)														
0.0000	646.07	0	0.2005	685.20	420	0.5098	753.10	526	0.8073	826.30	285	1.0000	878.24	0
0.0470	654.60	138	0.2579	697.20	473	0.6081	776.40	474	0.8511	837.70	242			
0.1095	666.70	296	0.2981	705.70	513	0.7112	801.80	388	0.9081	852.90	166			
0.1485	674.60	347	0.4033	728.80	540	0.7576	813.50	344	0.9598	867.30	46			
$T = 318.15$ K														
Ethyl Methanoate (1) + Hexane (2)														
0.0000	636.43	0	0.1471	655.88	904	0.5293	729.70	1440	0.7932	805.56	919			
0.0476	642.18	346	0.2199	667.46	1139	0.5869	744.10	1385	0.8873	840.19	541			
0.0875	647.84	511	0.3041	681.93	1374	0.6984	775.52	1146	0.9692	874.21	174			
0.1044	649.54	733	0.4061	701.97	1470	0.7476	790.78	1018	1.0000	888.42	0			
Propyl Methanoate (1) + Hexane (2)														
0.0000	636.43	0	0.2909	687.08	908	0.5747	750.24	889	0.7661	801.18	612	0.9581	860.97	126
0.0796	648.93	351	0.3611	701.46	957	0.6031	757.34	859	0.8123	814.59	527	1.0000	875.32	0
0.1547	661.76	602	0.4273	715.75	966	0.6617	772.47	785	0.8602	829.22	406			
0.2278	674.93	805	0.4870	729.26	949	0.7118	785.91	716	0.9109	845.53	241			
Butyl Methanoate (1) + Hexane (2)														
0.0000	636.43	0	0.1589	666.90	417	0.4015	718.00	620	0.7460	799.70	394	1.0000	867.21	0
0.0493	645.60	166	0.1975	674.70	475	0.4950	739.20	590	0.8134	817.05	296			
0.0857	652.70	229	0.2452	684.50	530	0.5929	762.20	525	0.9067	841.50	182			
0.1192	659.10	332	0.3006	696.20	567	0.7050	789.50	428	0.9647	857.10	110			

was also verified by measuring the relevant physical properties such as the boiling point $T^{\circ}_{\mathrm{b},i}$, density ρ, and refraction index n_{D} at temperatures of (298.15 and 318.15) K, except for the mixture with methyl methanoate. Since the latter has a normal boiling point $T^{\circ}_{\mathrm{b},i} < 318.15$ K, measurements were only obtained at 298.15 K. The experimental results obtained directly are shown in Table 1 and compared with data from the literature, showing acceptable discrepancies. Other parameters obtained indirectly are also presented and compared with those in the literature when they exist.

Apparatus and Procedures. The isobaric experimental VLE was measured in a small volume device described in previous papers.[1,3] It consists of a small glass ebulliometer of about 60 cm^3 capacity, operating continuously with phases recirculation. Pressure was controlled using a controller/calibrator, model PPC2, supplied by Desgranges et Huot, capable of maintaining a pressure at (101.32 ± 0.02) kPa during the entire measuring process. The temperature of both phases in equilibrium was measured with a digital thermometer from Comarks Electronics Ltd., model 6800, calibrated regularly according to ITS-90 and presenting an uncertainty of around ± 20 mK.

The concentrations of the two phases were determined with an Anton Paar densimeter, model DMA-55, with an uncertainty of ± 0.02 kg·m^{-3}. Samples of both phases were taken after the equipment reached a stationary state with constant pressure and temperature. The methanoate concentrations x and y were calculated from density concentration curves $\rho = \rho(x)$ previously determined for each mixture with synthetic samples of known composition at a temperature of $T = (298.15 \pm 0.01)$ K, using an equation of the form $\rho(x_1) = [(\rho_1 - \rho_2)x_1 + \rho_2] - [x_1(1 - x_1)(ax_1{}^2 + bx_1 + c)]$, where ρ, ρ_1, and ρ_2 are respectively the densities of the mixtures, the ester, and hexane. The concentrations of the liquid and vapor phases thus obtained present an uncertainty of ± 0.002 units. The measurements (x_1, ρ) for each of the studied mixtures over the entire range of concentrations allowed for calculating the values of the excess volumes $V^{\mathrm{E}}_{\mathrm{m}}$ with an uncertainty of $\pm\, 2{\cdot}10^9$ m^3·mol^{-1}, while the concentrations of the synthetic samples x_1 presented an uncertainty of $\pm\, 3{\cdot}10^{-4}$.

The excess enthalpies were determined at (291.15 and 318.15) K for the samples considered here, except for the system methyl methanoate + hexane, using a Calvet microcalorimeter, model MS80, by Setaram. The uncertainty of experimental results with this instrument was lower than ± 0.3 J·mol^{-1} for $H^{\mathrm{E}}_{\mathrm{m}}$. This estimation was made previously comparing the measurements obtained for the ethanol + nonane system and those from literature.[20] The concentrations of each point presented an uncertainty of $\pm\, 5{\cdot}10^{-4}$.

Results

Excess Properties. Table 2 shows the experimental data (x_1, $V^{\mathrm{E}}_{\mathrm{m}}$) obtained for the binary mixtures of alkyl methanoates (ethyl to butyl) (1) + hexane (2) at (291.15, 298.15, 308.15, and 318.15) K. For the mixture methyl methanoate + hexane, measurements were only made at (291.15 and 298.15) K, since the normal boiling temperature of methyl methanoate is $T^{\circ}_{\mathrm{b},i} = 304.7$ K. The same argument applies for the measurements of $H^{\mathrm{E}}_{\mathrm{m}}$, determined at temperatures of (291.15 and 318.15) K for mixtures of hexane with the other three methanoates (ethyl to butyl). The pertinent values are shown in Table 3. The $V^{\mathrm{E}}_{\mathrm{m}}$ and $H^{\mathrm{E}}_{\mathrm{m}}$ data were correlated with the molar fraction of methanoate using the following polynomial equation, which when applied to values of a generic function $Y^{\mathrm{E}}_{\mathrm{m}}$ as a function of concentration, has the form:

$$Y^{\mathrm{E}}_{\mathrm{m}} = z_1 z_2 \sum_{i=0}^{2} a_i z_1{}^{i} = z_1(1 - z_1)(a_0 + a_1 z_1 + a_2 z_1{}^2) \qquad (1)$$

where $z_1 = x_1/(x_1 + kx_2)$ is the active fraction of the compound in the binary mixture. In other words, z_1 corresponds to the

Table 3. Excess Molar Enthalpies H_m^E for Binary Systems of Alkyl Methanoate (1) + Hexane (2) at Two Different Temperatures

x_1	H_m^E / J·mol^{-1}	x_1	H_m^E / J·mol^{-1}	x_1	H_m^E / J·mol^{-1}
		$T = 291.15$ K			
		Methyl Methanoate (1) + Hexane (2)			
0.1408	1059.9	0.5501	2063.2	0.7971	1382.0
0.2520	1625.9	0.5862	2013.4	0.8450	1175.4
0.3379	1934.6	0.6157	1931.8	0.8923	916.9
0.4008	2058.2	0.6568	1836.4	0.9292	640.1
0.4618	2110.5	0.7033	1713.4	0.9665	374.8
0.5094	2098.6	0.7517	1546.7		
		Ethyl Methanoate (1) + Hexane (2)			
0.0920	448.8	0.5161	1539.9	0.7841	1015.9
0.2090	955.5	0.5681	1525.3	0.8430	787.1
0.3175	1274.2	0.6185	1437.6	0.9022	531.1
0.4075	1447.5	0.6714	1335.8	0.9514	305.2
0.4677	1522.9	0.7272	1198.6		
		Propyl Methanoate (1) + Hexane (2)			
0.0969	492.5	0.4458	1210.2	0.6905	964.0
0.1860	782.6	0.4941	1215.0	0.7533	814.7
0.2656	983.2	0.5356	1200.5	0.8171	643.2
0.3316	1105.3	0.5758	1148.3	0.8850	415.4
0.3921	1178.1	0.6321	1080.7	0.9453	191.6
		Butyl Methanoate (1) + Hexane (2)			
0.0865	321.7	0.4081	1037.9	0.6775	859.8
0.1588	562.4	0.4540	1056.9	0.7406	738.0
0.2303	764.2	0.5114	1051.2	0.8067	584.5
0.2973	905.2	0.5606	1017.7	0.8730	401.2
0.3551	989.7	0.6177	953.2	0.9400	212.8
		$T = 318.15$ K			
		Ethyl Methanoate (1) + Hexane (2)			
0.1003	622.3	0.5137	1647.0	0.8299	902.3
0.1895	1019.4	0.5599	1619.1	0.8814	646.8
0.2842	1352.0	0.5991	1565.8	0.9215	439.8
0.3713	1534.2	0.6795	1409.9	0.9660	213.2
0.4495	1627.9	0.7593	1175.2		
		Propyl Methanoate (1) + Hexane (2)			
0.0848	472.8	0.4624	1340.9	0.7368	1025.1
0.1889	845.7	0.5210	1338.6	0.8154	793.7
0.2934	1122.6	0.5945	1291.9	0.8906	518.0
0.3854	1275.7	0.6631	1190.3	0.9523	248.6
		Butyl Methanoate (1) + Hexane (2)			
0.0808	440.3	0.4464	1150.9	0.7075	916.1
0.1626	704.8	0.4882	1147.7	0.7904	730.6
0.2415	907.6	0.5104	1151.5	0.8680	505.7
0.3110	1035.6	0.5661	1114.9	0.9412	270.0
0.3823	1119.8	0.6300	1046.2		

"active" contribution of the compound referring the concentration, for the excess property studied, and at the same concentration. Therefore, the parameter k depends on the property to be correlated. For the function G_m^E/RT the parameter k is just one more parameter in the data fitting process (referred to as k_g), while for the properties V_m^E and H_m^E, it is assigned a physical value is calculated as described below. To fit the data (x_1, V_m^E), this parameter is represented as k_v and is calculated from the quotient of the molar volumes, $V_{m,i}^{\circ}(T)$ of each of the pure compounds i at the working temperature. The experimental data show that similar results are achieved when k_v is calculated as the quotient of volume parameters, r_i for each of the components i where $r_i = \sum \upsilon_k^{(i)} R_k$ in which $\upsilon_k^{(i)}$ is the whole number that corresponds to the number of groups in the molecule of compound i. Parameters R_k correspond to the van der Waals group volume parameters reported in Bondi.[21] Although similar results were obtained with this group contribution method, we calculate k_v using the molar volumes of the compounds because the empirical method does not take into account the structural change in the different types of compounds (such as the regioisomers) or the changes in working conditions (such as temperature).

The enthalpy of the mixtures resulting from molecular interactions and the energetic effect is directly related to the contact surfaces between the molecules. For the correlation of (x_1, H_m^E) the k parameter is designated k_h, and in this case it corresponds to the quotient of the molecular surfaces of the substances involved in the system. Hence, the k_h values are obtained from a k_v value weighted with the quotients of theoretical parameters of area q_i and volume r_i, as shown below:

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

where $q_i = \sum \upsilon_k^{(i)} Q_k$ and the Q_k values are the van der Waals group area parameters, described in Bondi.[21]

The second column in Table 4 reports the values of k_v and k_h calculated by this method for the four systems studied here. It is seen that there are slight differences with the theoretical values k_r and k_q, which become more pronounced with increasing temperature. This table also gives the coefficients a_i of eq 1, obtained by a least-squares procedure, and the standard deviations for each mixture, $\sigma(Y_m^E)$. To avoid confusion, Figures 1a and 2a show, respectively, the experimental dots of V_m^E and the fitting curves, the former corresponding to temperatures (291.15 and 318.15) K and the latter to (298.15 and 308.15) K. Figures 1b and 2b show the values of V_m^E ($x = 0.5$) as a function of u, $HCOOC_uH_{2u+1}$, according to Figures 1a and 2a, respectively, together with the values found in the literature given for purposes of comparison. A difference of V_m^E ($x = 0.5$) is observed for the mixture of ethyl methanoate + hexane at 318.15 K, obtained in a previous work,[3] with a value 6 % higher than the one recorded here. In contrast, the value determined by this work in the mixture methyl methanoate + hexane at 298.15 K is higher than that determined previously in our laboratory,[9] possibly due to using a different batch of reagent. Estimation of V_m^E from the density produced a pronounced change in error distribution. Only slight differences were found in the values of V_m^E of the other mixtures.

Similarly, it is possible to deduce some conclusions about the presentation and correlation of the excess enthalpies. Values of the parameters obtained for eq 1 are found in Table 4, which also give the values for mixtures of alkyl methanoates + hexane obtained in a previous work[9,12] by applying the same equation. The experimental values and calculated values are shown in Figure 3a, while Figure 3b shows the equimolar values corresponding to the three temperatures.

Some interesting conclusions can be drawn from the results obtained. On one hand, the expansive effects of the mixtures studied are noteworthy, as reflected by the positive value of the $(\partial V_m^E/\partial T)_{p,x}$ coefficient, indicating that the thermal expansion of the solution increases with temperature. The reduced expansion with increasing length of the alkyl chain of the methanoate can be explained among other reasons by the better accommodation of the molecules of inert solvent (hexane) between those of the ester. The same effects can be observed for the enthalpies, which are endothermic in all cases, and with $(\partial H_m^E/\partial T)_{p,x} > 0$. In spite of the fact that a previous work[9] demonstrated the presence of bonds by hydrogen bridges in the alkyl methanoates with self-association effects, these effects are not very important as compared to other predominant ones, such as van der Waals attractions and dipole−dipole forces. Specifically, self-association effects can be significantly observed in the mixture with methyl methanoate, although all the effects

Table 4. Coefficients and Standard Deviations, σ, Obtained Using Equation 1 To Correlate the Excess Properties V_m^E and H_m^E

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

binary mixture	k_r	k_v	a_0	a_1	a_2	$10^9\ \sigma(V_m^E)$ / $m^3 \cdot mol^{-1}$
		$T = 291.15$ K				
hexane (2) + methyl methanoate (1)	2.100	2.120	17111	−31534	18365	47
hexane (2) + ethyl methanoate (1)	1.597	1.627	9666	−15290	9520	20
hexane (2) + propyl methanoate (1)	1.289	1.343	5855	−8466	4753	18
hexane (2) + butyl methanoate (1)	1.080	1.143	3802	−5521	2984	9
		$T = 298.15$ K				
hexane (2) + methyl methanoate (1)	2.100	2.118	17017	−31733	19360	39
hexane (2) + ethyl methanoate (1)	1.597	1.626	8842	−11502	4739	12
hexane (2) + propyl methanoate (1)	1.289	1.343	4693	−3810	879	21
hexane (2) + butyl methanoate (1)	1.080	1.145	2494	−1466	−617	13
		$T = 308.15$ K				
hexane (2) + ethyl methanoate (1)	1.597	1.624	10505	−15710	9074	20
hexane (2) + propyl methanoate (1)	1.289	1.345	4939	−3802	993	11
hexane (2) + butyl methanoate (1)	1.080	1.147	3553	−4167	2324	11
		$T = 318.15$ K				
hexane (2) + ethyl methanoate (1)	1.597	1.624	11648	−18255	10957	37
hexane (2) + propyl methanoate (1)	1.289	1.345	6735	−8506	4413	15
hexane (2) + butyl methanoate (1)	1.080	1.150	4029	−4911	2781	15

$Y_m^E = H_m^E$ in $J \cdot mol^{-1}$

binary mixture	k_q	k_h	a_0	a_1	a_2	$\sigma(H_m^E)$ / $J \cdot mol^{-1}$
		$T = 291.15$ K				
hexane (2) + methyl methanoate (1)	1.894	1.906	16384.2	−26224.4	16538.0	13.4
hexane (2) + ethyl methanoate (1)	1.497	1.515	8337.3	−5258.0	649.3	19.0
hexane (2) + propyl methanoate (1)	1.237	1.272	6559.1	−3957.1	472.8	12.6
hexane (2) + butyl methanoate (1)	1.055	1.095	4414.8	482.0	−1859.1	10.0
		$T = 298.15$ K				
hexane (2) + methyl methanoate (1)[a]	1.894	1.905	16665.7	−26097.5	15871.5	19.1
hexane (2) + ethyl methanoate (1)[b]	1.497	1.515	9769.2	−9859.7	4934.4	11.3
hexane (2) + propyl methanoate (1)[a]	1.237	1.272	7994.4	-8031.1	4355.3	21.2
hexane (2) + butyl methanoate (1)[a]	1.055	1.096	6176.5	−5090.5	2767.2	12.1
		$T = 318.15$ K				
hexane (2) + ethyl methanoate (1)	1.497	1.514	9938.2	−8958.1	3160.4	11.7
hexane (2) + propyl methanoate (1)	1.237	1.273	7234.2	−4978.6	2048.4	14.3
hexane (2) + butyl methanoate (1)	1.055	1.100	6218.8	−4756.9	2810.9	14.5

[a] Coefficients obtained using experimental values from ref 9. [b] Coefficients obtained using experimental values from ref 12.

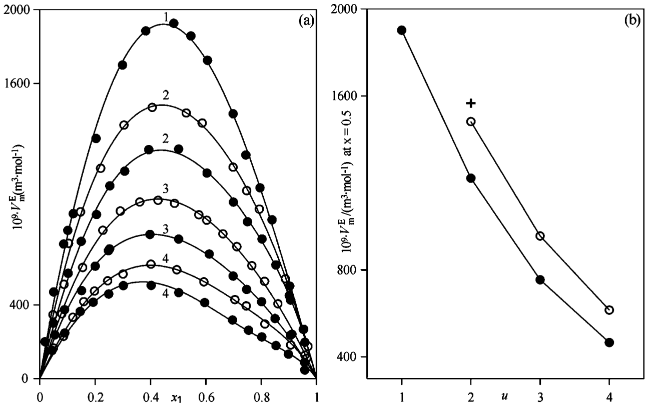

Figure 1. (a) Experimental values and correlation curves of V_m^E vs x_1 for binary mixtures $HCOO(CH_2)_{u-1}CH_3$ (1) + $CH_3(CH_2)_4CH_3$ (2). Labels indicate u values. (b) Variation of equimolar volume as a function of u and temperature: ●, at 291.15 K; ○, at 318.15 K; +, values from ref 3.

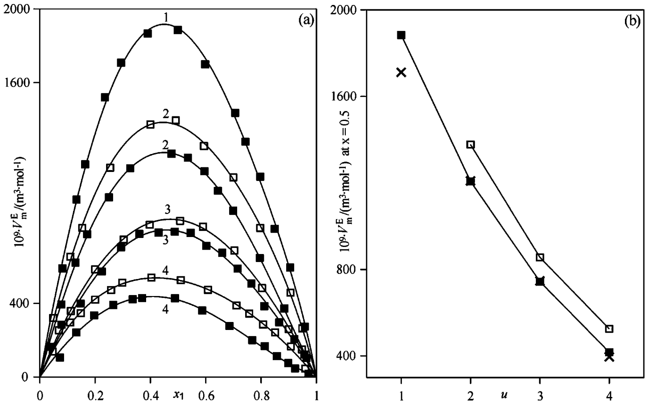

Figure 2. (a) Experimental values and correlation curves of V_m^E vs x_1 for binary mixtures $HCOO(CH_2)_{u-1}CH_3$ (1) + $CH_3(CH_2)_4CH_3$ (2). Labels indicate u values. (b) Variation of equimolar volume as a function of u and temperature: ■, at 298.15 K; □, at 308.15 K; ×, values from ref 9.

mentioned diminish with increased length of the alkanolic chain of the methanoate, reflected by the diminishing values of the properties studied (see Figures 1 to 3).

Vapor Pressures. The vapor pressure data used for pure compounds significantly affect the value that characterizes VLE, so it is usual to measure this property using the same experimental apparatus as that used for the VLE determination. Experimental values of (T, p_i^o) for the substances studied here have been obtained in our laboratory and reported in previous publications.[2,5−7,22] All of these were correlated with Antoine's equation, with the constants given in Table 5. Figure 4 shows the vapor pressure lines for the alkyl methanoates and hexane

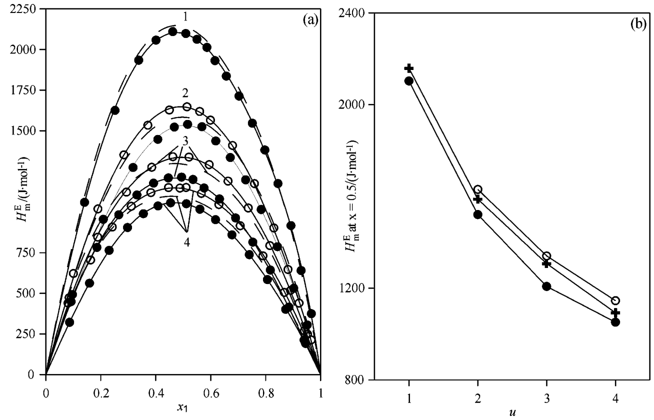

Figure 3. (a) Experimental values and correlation curves of H_m^E vs x_1 for binary mixtures $HCOO(CH_2)_{u-1}CH_3$ (1) + $CH_3(CH_2)_4CH_3$ (2). Labels indicate *u* values. ●, at 291.15 K; ○, at 318.15 K; − −, at 298.15 K (refs 9 and 12). (b) Variation of equimolar enthalpies as a function of *u* and temperature: ●, at 291.15 K; +, at 298.15 K; ○, at 318.15 K.

Table 5. Coefficients *A*, *B*, and *C* of the Antoine Equation, log(p_i°/kPa) = *A* − *B*/(*T*/*K*) − *C*] and Acentric Factors for Pure Compounds Used in This Work To Calculate the Activity Coefficients[a]

compound	*A*	*B*	*C*	*ω*	Δ*T*/K	ref
hexane	5.96291	1141.62	53.22	0.297	295−360	22
	(2.4828)	(2.2488)	(0.105)			22
methyl methanoate	6.45012	1216.46	31.08	0.258	300−330	5
	(3.0508)	(2.9595)	(0.013)			5
ethyl methanoate	6.65073	1431.31	19.09	0.273	300−350	2
	(2.9535)	(2.7897)	(0.040)			2
propyl methanoate	6.10108	1200.66	60.54	0.306	315−375	7
	(2.4738)	(2.2119)	(0.1148)			7
butyl methanoate	6.49980	1488.43	48.10	0.382	345−400	6
	(2.9533)	(2.6613)	(0.086)			6

[a] Between parentheses are the coefficients *a*, *b*, and *c* of the Antoine equation in the reduced form (eq 3).

in reduced coordinates using a similar expression to that of Antoine:

$$\log p_{i,r}^\circ = a - b/(T_r - c) \tag{3}$$

Table 5 reports in parentheses the values for *a*, *b*, and *c* obtained by applying a linear regression to the quantities (T_r, $p_{i,r}^\circ$) and using a least-squares procedure. Acentric factors were determined using their definition, $\omega = -(\log p_{i,r}^\circ)_{T_r=0.7} - 1$ and are also recorded in Table 5 and used in the treatment of equilibrium data.

Presentation of VLE Data. Table 6 reports values of (p, T, x_1, y_1) in isobaric VLE at p = (101.32 ± 0.02) kPa for the four binary systems $\{x_1HCOOC_uH_{2u+1}(u = 1 \text{ to } 4) + x_2C_6H_{14}\}$ studied here. Activity coefficients were calculated with

$$\ln \gamma_i = \ln\left(\frac{py_i}{p_i^\circ x_i}\right) + \frac{(B_{ii} - V_i^\circ)(p - p_i^\circ)}{RT} + \frac{p}{RT}\delta_{ij}y_j^2 \tag{4}$$

which takes into account the nonideality of the vapor phase. In eq 4, $\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$ and the second virial coefficients for the pure compounds (B_{ii}, B_{jj}) and their mixtures (B_{ij}) were estimated by Tsonopoulos's correlation.[23] This correlation contains a parameter *b*, the significance of which is exclusively associated with substances that present hydrogen bonds, although here a value of $b = 0$ has been used, in spite of the fact that methanoates present molecular association[9] in which case $b \neq 0$. This circumstance has not been taken into account in the estimation of the second virial coefficients of pure compounds and mixtures, since values currently published in the literature do not publish *b* values for esters, or more specifically, for methanoates. However, even when these are used, it is important to take into consideration that they only have a negligible effect on the final values of activity coefficients.

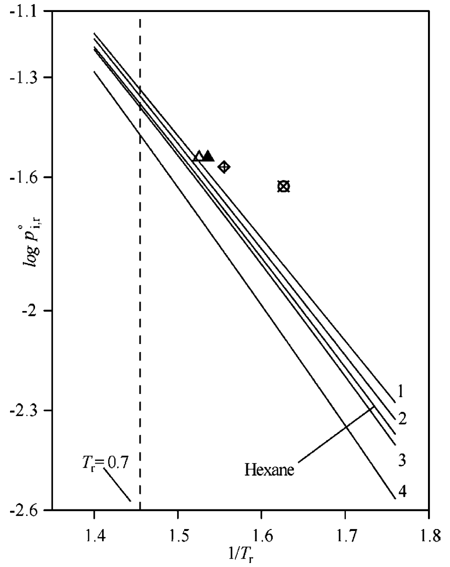

Figure 4. Vapor pressures lines in reduced coordinates for alkyl methanoates $HCOO(CH_2)_{u-1}CH_3$ and hexane. Labels indicate the *u* values. Situation of azeotropic point in reduced coordinates for the binary (methyl methanoate + hexane): ○, this work; ×, from ref 8; (ethyl methanoate + hexane): ◇, this work; +, from ref 3; and (propyl methanoate + hexane): △, this work; ▲, from ref 28.

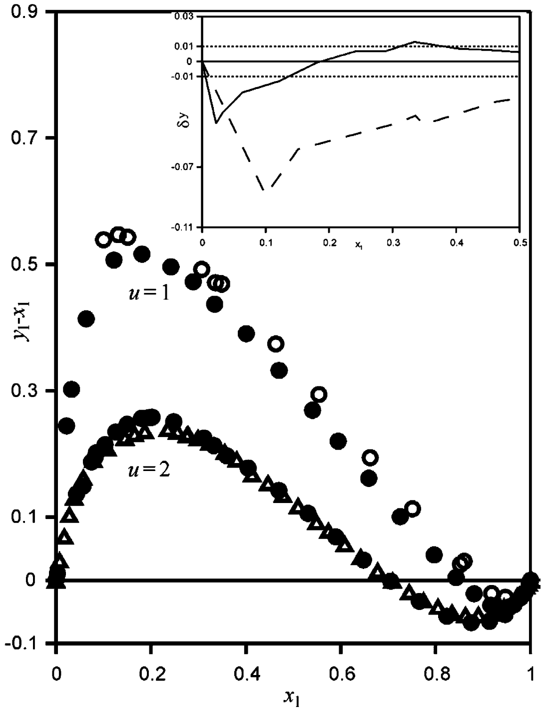

Figure 5. Representation of VLE experimental values ($y_1 - x_1$) vs x_1 for binary mixtures $HCOO(CH_2)_{u-1}CH_3$ (1) + $CH_3(CH_2)_4CH_3$ (2). Labels indicate *u* values. ●, this work; ○, from ref 8 for *u* = 1 and △, from ref 3 for *u* = 2. The inset figure shows the comparison between deviations δy_1 obtained in application of Fredenslund's method to our experimental values and those from ref 8 in the concentration range [0, 0.5].

Molar volumes V_i° of pure compounds at equilibrium temperatures are calculated with Rackett's equation, modified by Spencer and Danner,[24] using values of the Z_{RA} coefficient that appear in Reid et al.[25] The vapor pressures $p_{i,r}^\circ$ were calculated

Table 6. Experimental Data and Calculated Quantities for the Isobaric VLE of the Binary Mixtures of Alkyl Methanoate (1) + Hexane (2) at 101.32 kPa

T/K	x_1	y_1	γ_1	γ_2	G_m^E/RT	T/K	x_1	y_1	γ_1	γ_2	G_m^E/RT
Methyl Methanoate (1) + Hexane (2)											
341.76	0.0000	0.0000		1.000	0.000	303.08	0.6592	0.8204	1.325	2.055	0.431
333.45	0.0220	0.2663	4.826	0.969	0.004	302.91	0.7253	0.8257	1.219	2.491	0.395
331.00	0.0325	0.3347	4.406	0.962	0.011	302.77	0.7969	0.8369	1.130	3.172	0.332
325.36	0.0634	0.4771	3.810	0.943	0.030	302.73	0.8429	0.8473	1.084	3.847	0.279
315.65	0.1218	0.6286	3.556	1.009	0.163	302.75	0.8811	0.8597	1.051	4.669	0.227
311.55	0.1809	0.6971	3.046	1.030	0.226	302.88	0.9160	0.8763	1.025	5.799	0.171
308.20	0.2420	0.7380	2.705	1.096	0.311	303.07	0.9367	0.8903	1.012	6.774	0.132
306.72	0.2890	0.7615	2.462	1.128	0.346	303.36	0.9585	0.9172	1.008	7.715	0.092
305.93	0.3342	0.7711	2.217	1.193	0.384	303.85	0.9781	0.9501	1.005	8.646	0.052
304.76	0.4008	0.7910	1.977	1.269	0.416	304.11	0.9872	0.9657	1.002	10.068	0.032
303.99	0.4699	0.8020	1.758	1.403	0.444	304.55	0.9979	0.9921	1.003	13.898	0.008
303.53	0.5404	0.8095	1.569	1.586	0.455	304.70	1.0000	1.0000	1.000		0.000
303.30	0.5945	0.8146	1.447	1.766	0.450						
Ethyl Methanoate (1) + Hexane (2)											
341.76	0.0000	0.0000		1.000	0.000	325.60	0.3595	0.5566	1.637	1.160	0.272
341.41	0.0028	0.0134	3.076	0.998	0.001	324.84	0.4048	0.5823	1.560	1.207	0.292
337.13	0.0431	0.1796	3.047	0.986	0.035	324.22	0.4694	0.6114	1.448	1.287	0.306
335.90	0.0569	0.2058	2.748	1.006	0.064	323.81	0.5308	0.6366	1.347	1.381	0.309
334.85	0.0747	0.2620	2.752	0.985	0.062	323.53	0.5895	0.6580	1.265	1.500	0.305
334.37	0.0820	0.2763	2.684	0.989	0.071	323.38	0.6478	0.6798	1.195	1.646	0.291
334.12	0.0849	0.2867	2.711	0.986	0.071	323.31	0.7054	0.7038	1.139	1.825	0.269
332.97	0.1033	0.3178	2.561	0.998	0.095	323.39	0.7656	0.7323	1.089	2.068	0.236
331.63	0.1260	0.3608	2.488	1.002	0.116	323.66	0.8236	0.7667	1.050	2.373	0.193
330.46	0.1497	0.3964	2.388	1.010	0.139	324.11	0.8749	0.8078	1.025	2.716	0.147
329.30	0.1799	0.4361	2.270	1.017	0.161	324.67	0.9134	0.8483	1.012	3.040	0.107
328.72	0.1959	0.4535	2.209	1.025	0.175	325.38	0.9463	0.8920	1.003	3.409	0.068
328.48	0.2022	0.4603	2.189	1.028	0.181	325.93	0.9657	0.9271	1.002	3.537	0.046
327.17	0.2481	0.4991	2.020	1.058	0.217	326.56	0.9835	0.9619	1.000	3.764	0.022
326.06	0.3113	0.5365	1.795	1.110	0.254	326.94	0.9938	0.9847	1.000	3.973	0.009
325.85	0.3324	0.5455	1.721	1.131	0.263	327.33	1.0000	1.0000	1.000		0.000
Propyl Methanoate (1) + Hexane (2)											
341.76	0.0000	0.0000		1.000	0.000	340.85	0.6041	0.4490	1.126	1.430	0.213
341.25	0.0261	0.0413	2.375	0.998	0.021	341.25	0.6421	0.4725	1.100	1.497	0.205
340.72	0.0523	0.0796	2.324	1.001	0.045	341.82	0.6923	0.5007	1.060	1.620	0.189
340.25	0.0810	0.1159	2.219	1.005	0.069	342.56	0.7229	0.5280	1.044	1.664	0.172
339.74	0.1243	0.1623	2.059	1.015	0.103	344.00	0.7894	0.5875	1.014	1.834	0.139
339.35	0.1753	0.2085	1.900	1.031	0.138	345.05	0.8270	0.6324	1.007	1.930	0.119
339.12	0.2371	0.2532	1.719	1.059	0.172	346.01	0.8549	0.6698	0.999	2.010	0.101
339.10	0.3010	0.2924	1.564	1.096	0.199	347.25	0.8844	0.7163	0.992	2.092	0.079
339.20	0.3598	0.3243	1.446	1.140	0.216	348.45	0.9116	0.7641	0.988	2.199	0.059
339.37	0.4139	0.3524	1.357	1.187	0.227	349.55	0.9347	0.8115	0.988	2.307	0.044
339.64	0.4643	0.3777	1.285	1.238	0.231	350.67	0.9533	0.8545	0.985	2.413	0.027
340.07	0.5286	0.4084	1.202	1.320	0.228	352.60	0.9813	0.9370	0.988	2.475	0.005
340.42	0.5660	0.4300	1.168	1.367	0.224	353.92	1.0000	1.0000	1.000		0.000
Butyl Methanoate (1) + Hexane (2)											
341.76	0.0000	0.0000		1.000	0.000	357.40	0.7269	0.3649	1.014	1.494	0.120
342.03	0.0198	0.0133	2.383	0.997	0.014	358.87	0.7569	0.3941	0.999	1.541	0.105
342.36	0.0481	0.0288	2.097	1.001	0.036	360.60	0.7888	0.4340	0.996	1.584	0.094
342.84	0.0948	0.0531	1.925	1.011	0.072	362.78	0.8226	0.4801	0.982	1.637	0.072
343.43	0.1370	0.0736	1.805	1.020	0.098	365.52	0.8631	0.5498	0.979	1.715	0.055
344.42	0.2194	0.1071	1.579	1.056	0.142	368.22	0.8980	0.6258	0.981	1.790	0.042
345.84	0.2995	0.1373	1.405	1.091	0.163	371.76	0.9357	0.7322	0.985	1.866	0.026
347.23	0.3863	0.1661	1.251	1.156	0.175	374.24	0.9605	0.8169	0.991	1.959	0.018
348.83	0.4556	0.1986	1.195	1.197	0.179	376.08	0.9770	0.8824	0.995	2.071	0.012
349.97	0.5182	0.2216	1.125	1.272	0.177	377.36	0.9869	0.9299	0.998	2.104	0.008
351.93	0.5828	0.2609	1.097	1.320	0.170	378.49	0.9951	0.9718	1.000	2.206	0.004
353.35	0.6230	0.2872	1.073	1.355	0.159	380.13	1.0000	1.0000	1.000		0.000
355.27	0.6807	0.3218	1.028	1.445	0.137						

with Antoine's equation, using the constants *A*, *B*, and *C* of Table 5. With the activity coefficients obtained, values of Gibbs adimensional function $G_m^E = \sum x_i \ln \gamma_i$ were estimated and are reported in the last column of Table 6 for each binary system. The γ_i values show that the systems present a strong deviation from ideal values, especially for the methyl methanoate system (due to a greater molecular self-association). The deviation becomes less pronounced with increasing ester chain to give rise to a quasi-ideal behavior for butyl methanoate, producing a decreasing order of γ_i in the order methyl > ethyl > propyl > butyl.

The four systems studied satisfy the global condition suggested by Fredenslund,[26] $\bar{\delta} = \sum_i (y_{i,\mathrm{exp}} - y_{i,\mathrm{calc}})/N \leq 0.01$. Figure 5 shows the concentrations, in the form of $(y_1 - x_1)$ vs x_1, obtained for the binary systems {methyl methanoate (1) or ethyl methanoate (1) + hexane(2)} with the data recorded in the literature for comparative purposes. The differences found for the system (ethyl methanoate + hexane) between data from Table 6 and those obtained previously in our laboratory[3] are not significant. However, there are slight discrepancies for the mixture methyl methanoate + hexane with the values determined by Ogorodnikov et al.,[8] especially in the region of low

Table 7. Experimental Azeotropic Coordinates (x_{1az}, T_{az},) at p = 101.32 kPa for Binary Mixtures of Alkyl Methanoate (1) + Hexane (2) and Comparison with Those Found in Literature, and Values Predicted by Two Versions of the UNIFAC Model[15,16]

	x_{1az}, T_{az}/K		
mixture	exp	lit	ref
methyl methanoate (1) + hexane (2)	0.832, 302.62		this work
		0.849, 302.65	8
		non-azeotrope	27
		0.790, 301.54	15
		0.768, 300.25	16
ethyl methanoate (1) + hexane (2)	0.703, 323.32		this work
		0.709, 323.21	3
		0.703, 322.65	27
		0.660, 321.46	15
		0.651, 320.23	16
propyl methanoate (1) + hexane (2)	0.283, 339.10		this work
		0.290, 336.75	28
		0.196, 336.15	28
		0.306, 337.42	15
		0.336, 336.23	16

ester concentrations; these values do not verify with the consistency method proposed by Frendenslund et al.,[26] residual values are shown in the insert in Figure 5. Figure 6a−d shows the set of data obtained directly (T, x_1, y_1) for each binary system (x_1 alkyl methanoate $+x_2$hexane).Analysis of these gives rise to the following observations.

Three of the four systems studied present an azeotropic point, which is compared with the one reported in available compilations (Gmehling et al.,[27] Horsley[28]) in Table 7. For the mixture methyl methanoate +hexane the value is similar to that determined by Ogorodnikov et al.,[8] although Lecat (see Gmehling et al.[27]) estimated the nonexistence of an azeotrope for this mixture. In the mixture ethyl methanoate + hexane the values calculated in this work and those recorded in the literature are similar to those recorded by Gmehling et al.[27] The greatest difference is observed for the azeotrope calculated for the mixture propyl methanoate + hexane, especially at the temperatures reported in the literature. Figure 4 shows the situation of the azeotropic points using reduced coordinates, which have been represented together with the vapor pressure lines of the pure compounds in this work, alkyl methanoates and hexane. The pseudocritical properties were estimated as geometric mean of the critical properties of the pure compounds.

Figure 7a−d shows other characteristic values of VLE, such as γ_i and G_m^E/RT, as a function of the concentration of the corresponding alkyl methanoate x_1; the pertinent numerical values are given in Table 6. The correlation and prediction of these values is given below.

Treatment of VLE Data

The values of Gibbs function, $G_m^E = G_m^E(x_1,T)$, obtained for isobaric equilibrium were correlated by a simple mathematical equation already used in previous works[5−7] and having the following form:

$$\frac{G_m^E}{RT}(x_1, T) = z_1(1 - z_1)\sum_{i=0}^{m} a_i z_1^{\,i} \qquad (5)$$

where a_i can be written as a function of temperature, and z_1 is the active fraction of the corresponding methanoate in each of the binary mixtures that would be expressed as a function of the molar fraction of the same ester by a well-known relationship. However, for the correlation of Gibbs function (eq 5) with the temperature, it can be established that coefficients a_i are dependent on temperature as follows:

$$a_i = \sum_{j=0}^{3} A_{ij}T^{j-1} = \frac{A_{i0}}{T} + A_{i1} + A_{i2}T \qquad (6)$$

The number of coefficients A_{ij} in eq 6 can be reduced when over-parametrization is not required. After defining the adimen-

Table 8. Activity Coefficients at Infinite Dilution Obtained for Compounds in Binary Mixtures Alkyl Methanoate (1) + Hexane (2), Estimated by Equations 10 and 11

	methyl methanoate (1) + hexane (2)		ethyl methanoate (1) + hexane (2)	propyl methanoate (1) + hexane (2)	butyl methanoate (1) + hexane (2)
γ_1^∞	4.51	5.32[a]	3.10	2.52	2.23
γ_2^∞	11.84	12.08[a]	4.04	2.42	1.06

[a] Ref 29.

Table 9. Parameters for Equations 5 and 9 Obtained in Correlation of VLE Data of Binary Mixtures Alkyl Methanoate (1) + Hexane (2), and Standard Deviations Obtained for Activity Coefficients σ(ln γ_i), Nondimensional Gibbs Function $\sigma(G_m^E/RT)$, and Excess Enthalpies $\sigma(H_m^E)$ in J·mol^{-1}

	methyl methanoate (1) + hexane (2)	ethyl methanoate (1) + hexane (2)	propyl methanoate (1) + hexane (2)	butyl methanoate (1) + hexane (2)
A_{00}	−5.287	283.693	−17.520	−1521.303
A_{10}	259.651	−104.962	123.261	6992.515
A_{20}	−100.424	−718.935	0.837	2624.108
A_{01}	6.231	2.723	4.739	14.173
A_{11}	−4.152	−1.345	−4.919	−49.966
A_{21}	2.269	5.498	1.694	−13.608
A_{02}	−0.013	−0.007	−0.009	−0.028
A_{12}	0.006	0.004	0.010	0.083
A_{22}	−0.002	−0.009	−0.004	0.017
k	1.109	1.098	1.448	1.514
$\sigma(\ln \gamma_1)$	0.027	0.013	0.021	0.016
$\sigma(\ln \gamma_2)$	0.057	0.016	0.031	0.015
$\sigma(G_m^E/RT)$	0.021	0.012	0.009	0.009
$\sigma(H_m^E)$	38.9	7.2	16.1	20.2

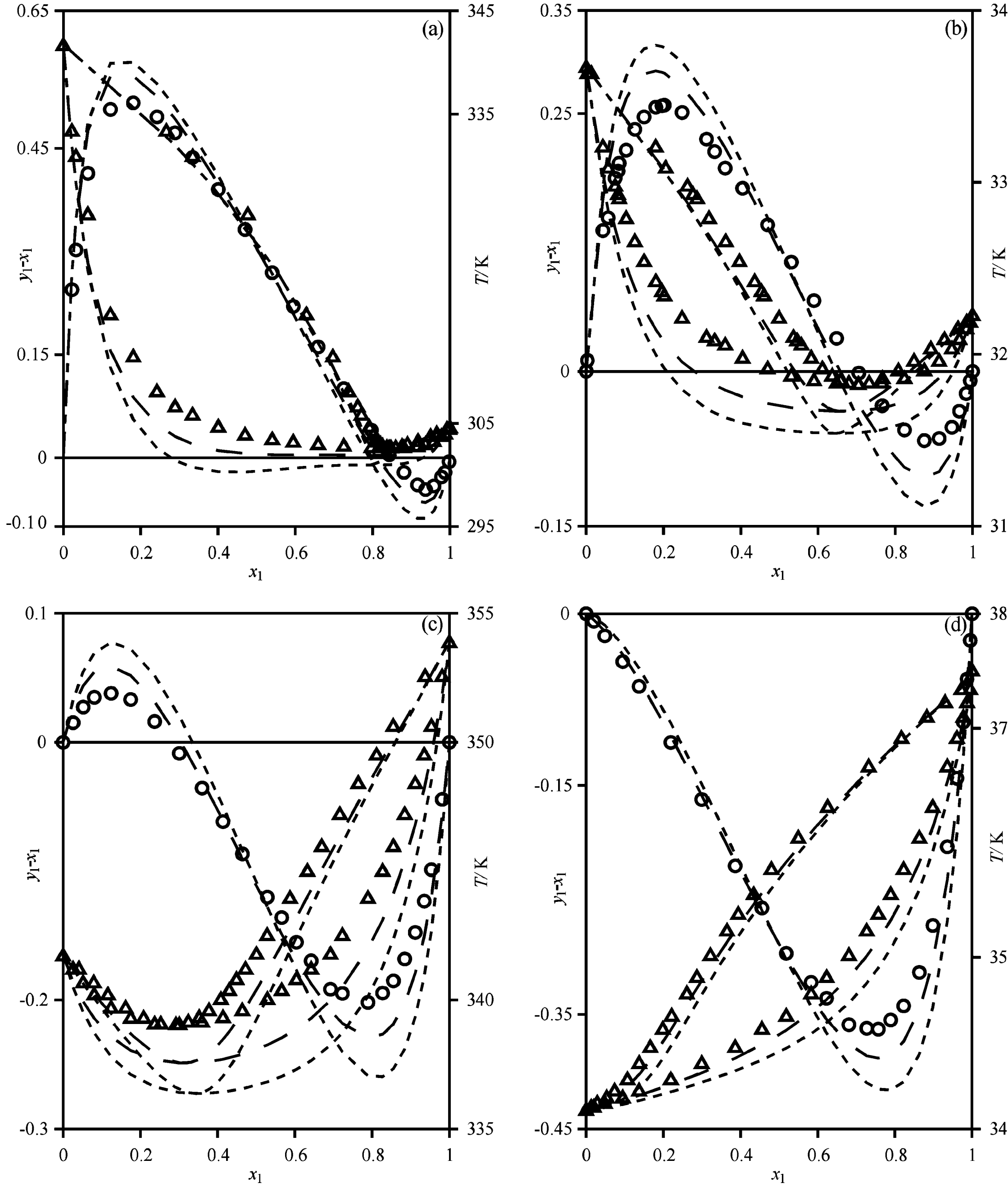

Figure 6. Representation of experimental VLE values: ○, ($y_1 - x_1$) vs x_1 and △, T vs x_1, y_1 for binary mixtures $HCOO(CH_2)_{u-1}CH_3$ (1) + C_6CH_{14} (2). (a) For $u = 1$. (b) For $u = 2$. (c) For $u = 3$. (d) For $u = 4$. Dashed lines represent the estimated curves with the UNIFAC model: — —, ref 15; - - -, ref 16.

sional Gibbs function as $Q = G^{E}_{m}/RT$, the mathematical expressions for enthalpies and activity coefficients must be obtained, considering the direct relationships between these quantities.

Hence, for the enthalpies we have the following relationship:

$$-\frac{H^{E}_{m}}{RT^{2}} = \left[\frac{\partial Q}{\partial T}\right]_{p,x} = z_1(1 - z_1)\sum_{i=0}^{2}\left(\frac{\mathrm{d}a_i}{\mathrm{d}T}\right)z_1^{\,i} + \left(\frac{\mathrm{d}z_1}{\mathrm{d}k}\right)\left(\frac{\mathrm{d}k}{\mathrm{d}T}\right)\left[(1 - 2z_1)\sum_{i=0}^{2} a_i z_1^{\,i} + z_1(1 - z_1)(a_1 + 2a_2 z_1)\right] \quad (7)$$

For the practical application of this equation, it can be assumed initially that the parameter k is independent of temperature, which would cancel out the second addenda of the expression (eq 7). To determine the activity coefficients, we know that in a binary mixture where $i = 1, 2$ and taking into account that $z_1 = z_1(x_1)$:

$$\ln \gamma_i = Q + (1 - x_i)\left(\frac{\partial Q}{\partial x_i}\right)_{p,T} = Q + (1 - x_i)\left(\frac{\partial Q}{\partial z_1}\right)\left(\frac{\mathrm{d}z_1}{\mathrm{d}x_i}\right) \quad (8)$$

which in our case produces the following generic equation:

$$\ln \gamma_i = z_1(1 - z_1)\sum_{i=0}^{2} a_i z_1^{\,i} + (1 - x_i)\left(\sum_{i=0}^{3}(i + 1)b_i\right)k\left(\frac{z_1}{x_1}\right)^2 \quad (9)$$

where $b_i = a_i - a_{i-1}$; y $0 \leq a_i \leq 3$. The corresponding values of the activity coefficients at infinite dilution can be determined, respectively, by

$$\ln \gamma_1^{\infty} = \lim_{x \to 0}\gamma_1 \equiv \lim_{z \to 0}\gamma_1 = \frac{a_0}{k} \quad (10)$$

$$\ln \gamma_2^{\infty} = \lim_{x \to 1}\gamma_2 \equiv \lim_{z \to 1}\gamma_2 = k(a_0 + a_1 + a_2) \quad (11)$$

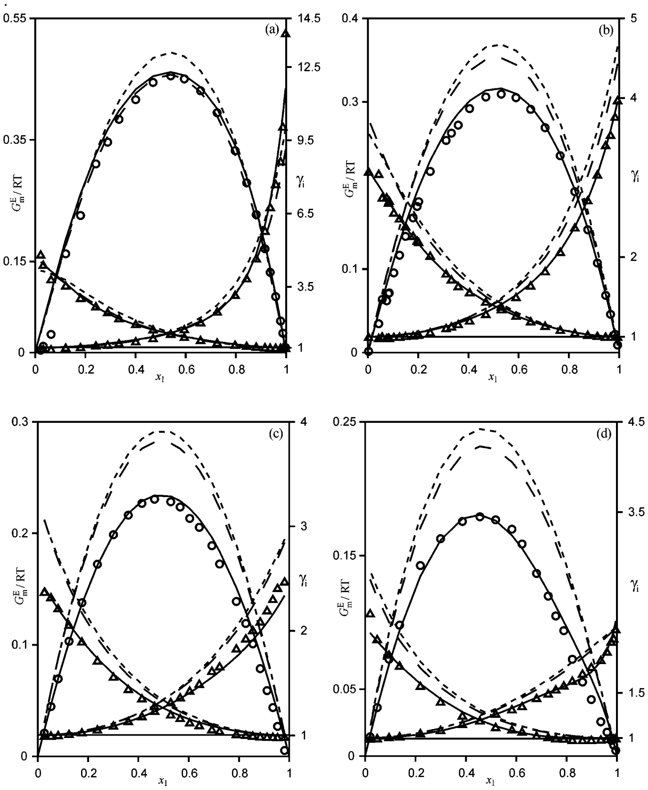

Figure 7. Representation of experimental and correlated curves (—) for quantities ○, G^E_m/RT vs x_1; △, γ_i vs x_1 for the binary mixtures HCOO(CH$_2$)$_{u-1}$ CH$_3$ (1) + C_6CH_{14} (2). (a) For $u = 1$. (b) For $u = 2$. (c) For $u = 3$. (d) For $u = 4$. Dashed lines represent the values estimated by the UNIFAC model: — —, ref 15; - - -, ref 16.

Table 8 shows that the values obtained for the mixtures alkyl methanoates + hexane present high values of γ_i^∞, especially in the methyl methanoate mixture (estimated values are similar to those published in the literature[29]), giving maximum values of nonideality in this case due to associative problems of the methanoate, which are most pronounced in methyl methanoate, steadily decreasing with increased alkanolic chain length as shown previously.

The set of eqs (5 to 9) allows the simultaneous correlation of experimental data with those data obtained from direct experimentation, such as the ln γ_i, data of the adimensional Gibbs function G^E_m/RT, and the enthalpies, also in adimensional form, H^E_m/RT. If direct experimental values of ln γ_i^∞ are known, these could be added to the corresponding algorithm and their values introduced in the objective function produced.

One important aspect to take into account for optimum correlation of the experimental data is the definition of objective function (OF). To minimize the OF, this should take into account the discrepancies between experimental values and theoretical ones, in other words, the enthalpies H^E_m, and logarithms of the activity coefficients ln γ_i. Since the Gibbs adimensional function is obtained from the activity coefficients and this has a statistically insignificant effect on the OF, it is not included in the proposed optimization equation:

$$OF = c_1\sigma(\ln\gamma_1) + c_2\sigma(\ln\gamma_2) + c_3\sigma(H^E_m) \qquad (12)$$

where $\sigma(\ln\gamma_i)$ and $\sigma(H^E_m)$, respectively, are the standard deviations of the activity coefficients and the excess enthalpies, generically defined as

$$\sigma(E) = [\sum_{i=1}^{n}(E_{i,\mathrm{exp}} - E_{i,\mathrm{cal}})^2/(n-1)]^{1/2} \qquad (13)$$

where E represents the values of the amounts considered and n the number of experiments. The coefficients c_i are used to compensate for the quantities introduced in the OF. Afterward, the data for each of the binary systems were correlated by

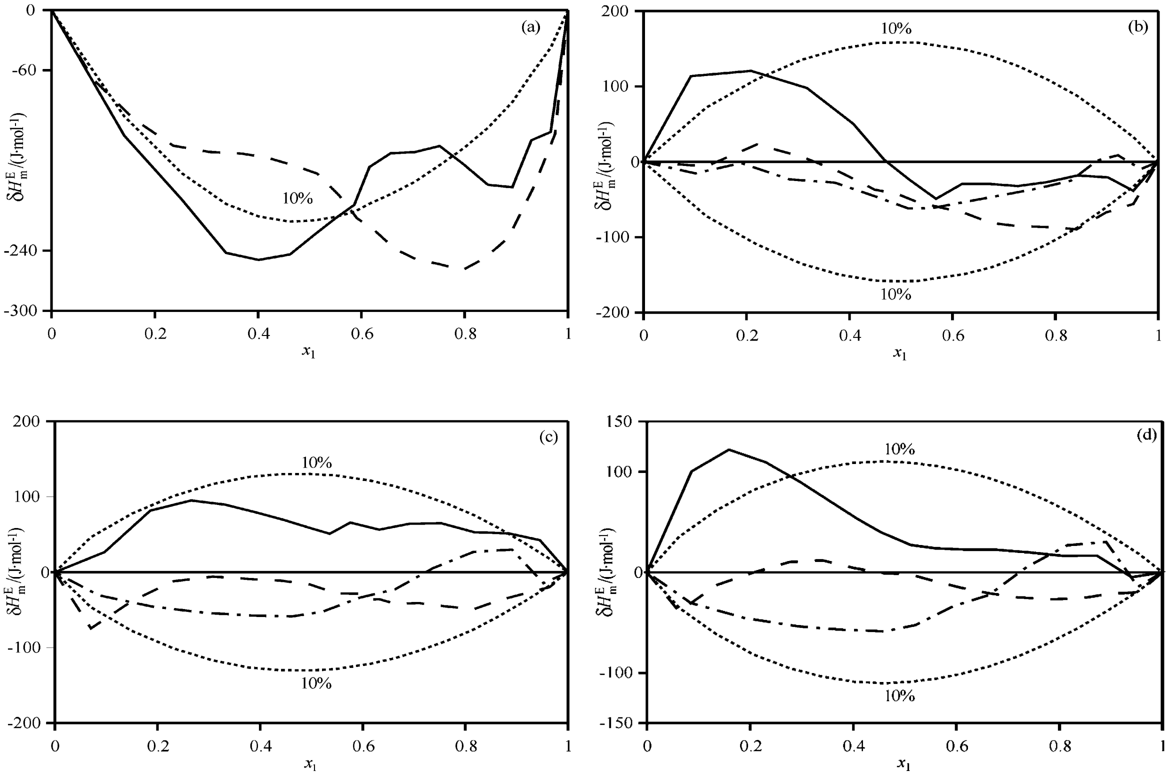

Figure 8. Representation of deviations $\delta H^E_m = H^E_{i,\mathrm{calc}} - H^E_{i,\mathrm{exp}}$ obtained for each experimental concentration as the differences between the estimated values by UNIFAC model[16] and those experimental values: —, at 291.15 K; — —, at 298.15 K; — · —, at 318.15 K.

programming the previous equations with an algorithm in MATLAB. The pertinent numerical results are reported in Table 9. This table shows that the A_{i2} coefficients of the first three binary systems do not make a significant contribution, implying that eq 6, as proposed here, can only be used to correlate data of the system butyl methanoate + hexane with an over-parametrization in the other three cases. Coefficients are included in Table 9 to demonstrate this fact and to standardize the correlations of the systems studied. The quantitative evaluation for the different systems is done by the calculating standard deviations of data, which are considered to be acceptable in all cases. Qualitatively, the data are shown in Figure 7a−d together with the experimental values where these can be obtained.

VLE Predictions. Two versions of the UNIFAC group contributions model have been used. The original version proposed by Fredenslund et al.[26] with the set of more recent parameters proposed by Hansen et al.[15] capable of estimating the γ_i of our systems and the version of Gmehling et al.[16] for which the γ_i can also be used to achieve the enthalpies of the mixture with a same set of interaction parameters. The results obtained for the four mixtures studied in this work with both theoretical models are displayed in Figure 7a−d, where they are graphically compared with experimental data. Likewise, Figure 6a−d shows the estimations made for the concentrations ($y_1 - x_1$) versus x_1 and for the temperatures T versus x_1, with y_1 values obtained starting with a given concentration x_1. Several observations can be made about this set: the two versions of the UNIFAC model used here produce very similar estimations, although they give results different from experimental values, and these differences increase as the chain length of methanoate increases. It can be also observed that the system methyl methanoate + hexane presents the best predictions of the activity coefficients and Gibbs adimensional function, possibly due to the use of VLE data from this binary system, the only one existing in the literature at that time to determine pairs of interaction parameters CH_2/HCOO. Therefore, with only the odd exception, there are important discrepancies in the estimations of azeotropic points as can be observed in Table 7. However, estimation of the enthalpies with Gmehling's et al. version[16] is not very deficient, with mean differences compared to experimental values of around 10 %, although the interaction parameters are inadequate. Figure 8a−d shows differences between experimental values and values calculated with the model and the curve, corresponding to a difference of 10 %, for comparative purposes. In summary, none of the UNIFAC versions can currently be recommended to represent thermodynamic properties of systems that are characterized by the CH_2/HCOO interaction. In future works, with a wider database, we will try to improve the model.

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