Thermodynamic properties of (a methyl ester + an *n*-alkane)

III. H_m^E and V_m^E for $\{xCH_3(CH_2)_{u-1}CO_2CH_3$ $(u = 1$ to $6) + (1-x)CH_3(CH_2)_8CH_3\}$

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The excess molar thermodynamic properties H_m^E and V_m^E of $\{xCH_3(CH_2)_{u-1}CO_2CH_3$ $(u = 1$ to $6) + (1-x)CH_3(CH_2)_8CH_3\}$ have been determined experimentally at the temperature 298.15 K. The general behaviour is similar to that of other (an ester + an alkane) mixtures, the values of H_m^E and V_m^E being positive for all these mixtures at all mole fractions. Both decrease quasi-regularly as the ester chain-length increases. The results are analysed in terms of several group-contribution theories.

1. Introduction

Continuing a series of investigations into the thermodynamic behaviour of binary mixtures of (an alkyl ester + an *n*-alkane with an even number of carbon atoms),[1, 2] the present paper reports the experimental excess molar enthalpies H_m^E and excess molar volumes V_m^E for six instances of {a methyl ester (from ethanoate to heptanoate) + decane} at the temperature 298.15 K. No H_m^E values were found in the literature for the mixtures considered at the pressure and temperature conditions employed in the experiments. However, V_m^E values were reported by Grolier *et al.*[3] and Awwad and Ibara[4] for (methyl ethanoate + decane), by Pintos *et al.*[5] for (methyl propanoate + decane), and by Ilic *et al.*[6] for (methyl butanoate + decane). The experimental results were analysed in terms of various group-contribution theories.

2. Experimental

The methyl esters employed were the same as those used in previous work, and their physical properties did not differ significantly from the values published earlier.[7, 8] The decane (Fluka AG, purum >0.99) was degassed and then dried on a 0.3 nm molecular sieve, also from Fluka. The physical characteristics of this aliphatic

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TABLE 1. Experimental H_m^E values for (a methyl ester + decane) at the temperature 298.15 K

x	$\dfrac{H_m^E}{J \cdot mol^{-1}}$	$\dfrac{\delta H_m^E}{J \cdot mol^{-1}}$	x	$\dfrac{H_m^E}{J \cdot mol^{-1}}$	$\dfrac{\delta H_m^E}{J \cdot mol^{-1}}$	x	$\dfrac{H_m^E}{J \cdot mol^{-1}}$	$\dfrac{\delta H_m^E}{J \cdot mol^{-1}}$
			$x CH_3 CO_2 CH_3 + (1-x) CH_3(CH_2)_8 CH_3$					
0.0948	649.2	2.7	0.5114	2068.7	5.8	0.8168	1377.0	−0.2
0.1735	1100.4	0.2	0.5503	2067.3	6.6	0.8578	1165.6	3.4
0.2384	1417.5	3.9	0.5814	2045.4	4.2	0.8962	931.4	5.5
0.3020	1661.8	−2.6	0.6466	1943.3	−5.8	0.9300	678.5	−3.1
0.3597	1835.0	−6.2	0.7007	1815.2	−4.5	0.9598	423.8	−3.9
0.4166	1963.6	−3.0	0.7458	1678.0	2.9	0.9839	187.5	1.7
0.4641	2031.3	−1.4	0.7798	1538.5	−4.9			
			$x CH_3 CH_2 CO_2 CH_3 + (1-x) CH_3(CH_2)_8 CH_3$					
0.0788	452.0	11.7	0.5483	1696.7	15.2	0.8275	1054.4	9.1
0.1590	833.9	−0.3	0.5794	1668.3	6.2	0.8638	890.8	8.1
0.2376	1153.9	−3.1	0.6303	1592.1	−10.1	0.8947	727.1	1.5
0.3137	1394.1	−7.9	0.6749	1512.1	−9.1	0.9241	551.8	−5.0
0.3830	1555.0	−6.7	0.7080	1432.6	−11.8	0.9558	342.3	−6.8
0.4467	1653.0	0.8	0.7453	1335.8	−4.7	0.9796	168.3	−2.9
0.5028	1696.6	10.7	0.7875	1206.2	5.4			
			$x CH_3 (CH_2)_2 CO_2 CH_3 + (1-x) CH_3(CH_2)_8 CH_3$					
0.0862	426.0	1.1	0.5035	1373.0	−1.2	0.7456	1065.9	−2.0
0.1769	752.3	−5.1	0.5450	1367.6	−2.5	0.7945	920.0	−2.4
0.2673	1035.6	1.4	0.5917	1336.5	−5.2	0.8396	769.1	6.0
0.3387	1204.7	5.1	0.6293	1295.6	−4.8	0.8867	583.6	12.8
0.4092	1315.6	4.6	0.6653	1240.3	−5.2	0.9305	382.7	14.3
0.4630	1363.5	4.2	0.7035	1165.3	−5.2	0.9690	184.7	13.3
			$x CH_3 (CH_2)_3 CO_2 CH_3 + (1-x) CH_3(CH_2)_8 CH_3$					
0.0744	323.4	9.7	0.4919	1142.9	4.2	0.7221	911.8	−2.5
0.1577	600.5	−4.7	0.5355	1136.4	3.1	0.7738	799.1	1.6
0.2421	833.6	−2.4	0.5690	1113.5	−3.8	0.8256	661.8	5.8
0.3225	989.1	−6.4	0.6007	1090.3	−2.5	0.8757	503.8	7.8
0.3883	1080.7	−1.5	0.6365	1053.6	−0.5	0.9232	331.2	8.2
0.4416	1122.7	−0.8	0.6765	995.7	−1.4	0.9665	159.3	11.8
			$x CH_3 (CH_2)_4 CO_2 CH_3 + (1-x) CH_3(CH_2)_8 CH_3$					
0.0521	214.0	5.1	0.4410	978.9	4.0	0.7375	741.7	−1.1
0.1098	403.5	−4.7	0.4837	987.2	4.7	0.7924	628.6	0.3
0.1708	580.9	−3.1	0.5236	981.7	4.8	0.8444	502.3	2.4
0.2322	726.7	−0.3	0.5472	958.6	−9.3	0.8922	370.0	5.4
0.2909	834.1	1.1	0.6107	916.5	−6.3	0.9324	243.4	5.1
0.3478	910.3	2.0	0.6479	878.4	−3.9	0.9687	120.8	6.5
0.3955	953.1	2.1	0.6896	823.1	−1.6			
			$x CH_3 (CH_2)_5 CO_2 CH_3 + (1-x) CH_3(CH_2)_8 CH_3$					
0.0499	207.1	−1.2	0.4308	882.1	1.4	0.7440	651.2	−3.0
0.1060	392.2	0.2	0.4898	887.2	−0.1	0.7939	560.6	1.1
0.1641	542.8	−0.5	0.5399	867.9	−6.8	0.8399	461.8	3.8
0.2226	664.9	1.1	0.5738	855.7	−1.1	0.8849	349.3	3.5
0.2798	755.5	0.6	0.6098	830.3	0.7	0.9266	233.0	2.8
0.3348	820.2	0.8	0.6501	788.5	−0.6	0.9658	114.9	3.4
0.3814	858.8	1.7	0.6961	730.4	0.3			

TABLE 2. Experimental V_m^E values for (a methyl ester + decane) at the temperature 298.15 K

x	$\dfrac{V_m^E}{cm^3 \cdot mol^{-1}}$	$\dfrac{10^3 \cdot \delta V_m^E}{cm^3 \cdot mol^{-1}}$	x	$\dfrac{V_m^E}{cm^3 \cdot mol^{-1}}$	$\dfrac{10^3 \cdot \delta V_m^E}{cm^3 \cdot mol^{-1}}$	x	$\dfrac{V_m^E}{cm^3 \cdot mol^{-1}}$	$\dfrac{10^3 \cdot \delta V_m^E}{cm^3 \cdot mol^{-1}}$
			$xCH_3CO_2CH_3 + (1-x)CH_3(CH_2)_8CH_3$					
0.0377	0.240	1	0.4618	1.611	1	0.7520	1.329	4
0.0846	0.504	−3	0.4979	1.628	1	0.7773	1.246	−4
0.1507	0.833	−0	0.5290	1.632	3	0.8043	1.159	−0
0.1907	1.005	4	0.5814	1.608	−1	0.8350	1.038	−3
0.2389	1.177	1	0.6174	1.578	0	0.8645	0.912	2
0.3099	1.378	−1	0.6619	1.516	−3	0.8870	0.799	2
0.3615	1.485	−3	0.6946	1.464	4	0.9125	0.651	−3
0.4196	1.570	−3	0.7134	1.420	−1	0.9588	0.346	3
			$xCH_3CH_2CO_2CH_3 + (1-x)CH_3(CH_2)_8CH_3$					
0.0413	0.194	−0	0.5144	1.256	2	0.7645	0.972	−2
0.1053	0.465	4	0.5567	1.250	1	0.7923	0.904	2
0.2030	0.791	−1	0.6009	1.227	1	0.8336	0.776	−2
0.2509	0.923	2	0.6101	1.215	−3	0.8410	0.750	−4
0.2963	1.020	−4	0.6639	1.160	−1	0.8705	0.650	2
0.4439	1.227	0	0.7324	1.045	−0	0.9191	0.443	0
0.4546	1.233	−1	0.7388	1.036	4	0.9486	0.299	1
			$xCH_3(CH_2)_2CO_2CH_3 + (1-x)CH_3(CH_2)_8CH_3$					
0.0573	0.218	−2	0.3461	0.913	−1	0.7493	0.784	−1
0.0812	0.308	4	0.3995	0.965	−0	0.8067	0.666	−0
0.1496	0.515	−4	0.4573	0.992	−4	0.8330	0.601	−1
0.2054	0.666	1	0.5126	1.003	0	0.8988	0.406	−2
0.2463	0.755	0	0.5758	0.987	3	0.9281	0.306	1
0.3089	0.867	3	0.6388	0.937	−0	0.8705	0.137	2
0.3295	0.894	1	0.7026	0.861	1			
			$xCH_3(CH_2)_3CO_2CH_3 + (1-x)CH_3(CH_2)_8CH_3$					
0.0297	0.101	1	0.4135	0.755	1	0.7278	0.606	−3
0.0681	0.217	−0	0.4706	0.770	1	0.7445	0.586	0
0.1205	0.354	−2	0.4786	0.766	−3	0.7906	0.516	4
0.1659	0.457	1	0.5113	0.766	−1	0.8305	0.440	2
0.2531	0.609	1	0.5508	0.761	2	0.8629	0.366	−4
0.2590	0.617	1	0.6178	0.723	1	0.9208	0.232	2
0.3316	0.697	−2	0.6414	0.702	−2	0.9576	0.128	−2
			$xCH_3(CH_2)_4CO_2CH_3 + (1-x)CH_3(CH_2)_8CH_3$					
0.0930	0.237	−2	0.3707	0.592	2	0.7485	0.444	0
0.1200	0.300	2	0.3937	0.597	−3	0.7884	0.401	9
0.1477	0.354	3	0.4532	0.618	5	0.8270	0.336	2
0.1608	0.373	−0	0.4973	0.614	1	0.8499	0.291	−7
0.1840	0.410	−0	0.5041	0.610	−1	0.8696	0.262	−2
0.2039	0.439	−0	0.6727	0.527	3	0.9009	0.201	−7
0.2455	0.486	−5	0.7000	0.493	−5	0.9602	0.088	−0
			$xCH_3(CH_2)_5CO_2CH_3 + (1-x)CH_3(CH_2)_8CH_3$					
0.0386	0.089	−1	0.3927	0.482	−1	0.7949	0.298	−2
0.0782	0.170	−2	0.4560	0.488	−2	0.8248	0.264	1
0.1273	0.258	1	0.4847	0.485	−4	0.8811	0.188	2
0.2031	0.361	1	0.5537	0.479	5	0.8914	0.172	2
0.2286	0.387	0	0.6006	0.460	5	0.9509	0.077	0
0.2603	0.417	2	0.6947	0.395	−1	0.9688	0.044	−4
0.3146	0.452	−1	0.7159	0.377	−2			
0.3524	0.471	0	0.7482	0.347	−2			

TABLE 3. Parameters A_i and standard deviations s obtained for equation (1)

Mixture	k	A_0	A_1	A_2	A_3	
		$Y^E = H_m^E/(J \cdot mol^{-1})$				s
$(1-x)CH_3(CH_2)_8CH_3 +$						
$xCH_3CO_2CH_3$	2.700	7366.2	4780.1	−7962.7	8067.6	4.5
$xCH_3CH_2CO_2CH_3$	1.893	5876.3	4753.3	−9011.1	7249.4	8.8
$xCH_3(CH_2)_2CO_2CH_3$	0.066	9614.3	−11852.7	7953.7	—	7.3
$xCH_3(CH_2)_3CO_2CH_3$	0.190	4556.0	—	—	—	5.6
$xCH_3(CH_2)_4CO_2CH_3$	0.449	4288.6	−524.0	—	—	4.6
$xCH_3(CH_2)_5CO_2CH_3$	0.142	4777.8	−1408.6	—	—	2.5
		$Y^E = V_m^E/(cm^3 \cdot mol^{-1})$				$10^3 \cdot s$
$(1-x)CH_3(CH_2)_8CH_3 +$						
$xCH_3CO_2CH_3$	2.146	6.614	−1.718	4.358	—	2.6
$xCH_3CH_2CO_2CH_3$	2.014	4.908	−0.298	1.799	—	2.4
$xCH_3(CH_2)_2CO_2CH_3$	0.952	4.038	0.665	−2.967	3.073	2.3
$xCH_3(CH_2)_3CO_2CH_3$	0.972	3.516	−1.467	1.177	—	2.1
$xCH_3(CH_2)_4CO_2CH_3$	0.046	−0.143	8.454	−6.006	—	4.0
$xCH_3(CH_2)_5CO_2CH_3$	2.176	2.487	−3.033	5.199	−3.197	2.5

hydrocarbon at the temperature 298.15 K were: $\rho/(kg \cdot m^{-3}) = 726.13$, 726.15;[5] $n_D = 1.4098$, 1.40967.[9]

Changes in enthalpy values for the mixtures were measured using a Calvet microcalorimeter according to a method described earlier.[1] The excess molar volumes were determined from densities for the pure components and their mixtures, measured with an Anton-Paar model DMA 60/602 densimeter thermostatted at the temperature (298.15 ± 0.01) K according to a method previously described. Values for other characteristic quantities for the pure components are also required so as to be able to apply certain of the theories employed herein. Accordingly, a piezometric method[10] was used to determine the isothermal compressibility κ_T and isobaric expansivity α for decane at the temperature 298.15 K. The values were $\kappa_T/kPa^{-1} = 1.095 \cdot 10^{-6}$, $1.094 \cdot 10^{-6}$,[9] and $\alpha/K^{-1} = 1.041 \cdot 10^{-3}$, $1.041 \cdot 10^{-3}$.[9] The values for these quantities for the methyl esters were published in an earlier paper.[2]

3. Results and discussion

Tables 1 and 2 present, respectively, the experimental H_m^E and V_m^E values for the six mixtures: $\{xCH_3(CH_2)_{u-1}CO_2CH_3 + (1-x)CH_3(CH_2)_8CH_3\}$ at the temperature 298.15 K. For both quantities the differences were determined using the experimental values and those estimated from a variable-degree polynomial of the form:

$$Y^E = x(1-x) \sum_{i=1}^{j} A_i[x/\{x+k(1-x)\}]^{i-1}, \qquad (1)$$

Y^E being $H_m^E/(J \cdot mol^{-1})$ or $V_m^E/(cm^3 \cdot mol^{-1})$, and where j was the total number of parameters, determined using an F-test, used to fit the experimental values for each mixture. In addition, the best value of k for each degree of the polynomial was
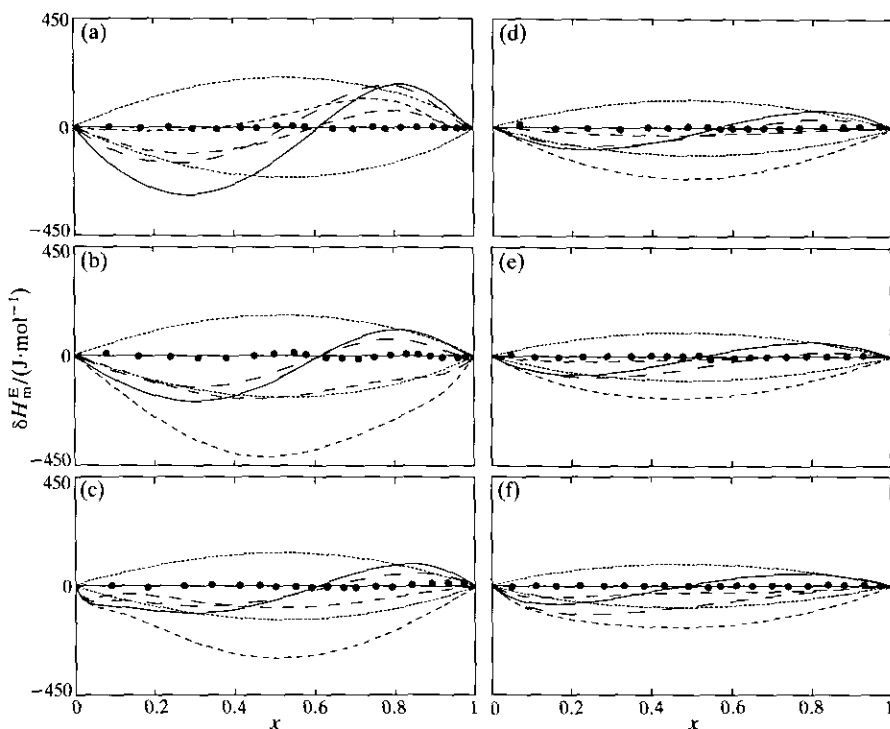
FIGURE 1. Deviations, $\delta H_m^E = (H_m^E - H_{m,\text{calc}}^E)$ from equation (1) of the experimental values for $\{xCH_3(CH_2)_{u-1}CO_2CH_3 + (1-x)CH_3(CH_2)_8CH_3\}$ at the temperature 298.15 K. (a), $u = 1$; (b), $u = 2$; (c), $u = 3$; (d), $u = 4$; (e), $u = 5$; (f), $u = 6$. ●, Our experimental results; ------, curves corresponding to $\pm 0.10 \cdot H_m^E$; — — — —, UNIFAC-1; ———, UNIFAC-2; ————, Nitta *et al.*;[14] ————, Flory.[15]

obtained by optimizing the standard deviations s for the fits. The A_i and s values for each mixture are set out in table 3. Both H_m^E and V_m^E are positive over the entire mole-fraction range, and the comparison between the experimental and literature values is described below. For (methyl ethanoate + decane), our results showed good agreement with those of Grolier *et al.*,[3] with a mean error $< |0.025 \cdot V_m^E|$ for all points; the differences with respect to the values published by Awwad and Ibara[4] were somewhat higher, with a mean error $< |0.04 \cdot V_m^E|$. The V_m^E values for (methyl propanoate + decane) presented by Pintos *et al.*[5] differed from our values by slightly more than $|0.05 \cdot V_m^E|$; and the mean error between our values and the values reported by Ilic *et al.*[6] for (methyl butanoate + decane) was $< |0.03 \cdot V_m^E|$.

Several group-contribution methods (see Ortega *et al.*)[1,2] were used to estimate the H_m^E values. Plotting all the curves for our experimental results fitted by equation (1) would result in a figure that would be very difficult to interpret. Therefore, figure 1 (a to f) shows the differences δH_m^E between the values for each mixture calculated using equation (1) and the values calculated using each of the theories. UNIFAC-1[11] yielded a mean estimation error $< |0.05 \cdot H_m^E|$ for the H_m^E values for the six mixtures considered herein. For UNIFAC-2[12] the error was $|0.17 \cdot H_m^E|$, though
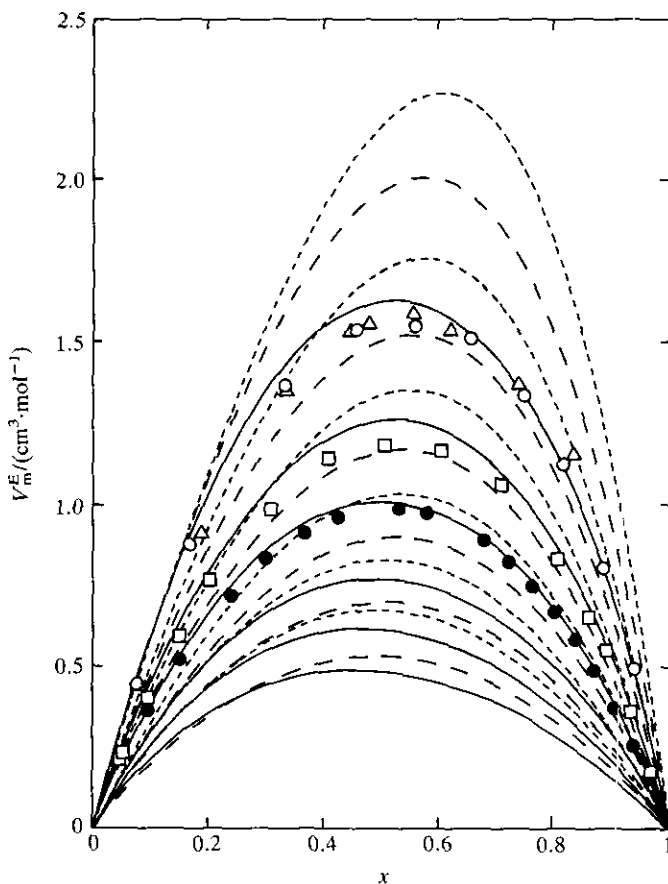
FIGURE 2. Comparison of experimental and theoretical values of V_m^E for $\{xCH_3(CH_2)_{u-1}CO_2CH_3 + (1-x)CH_3(CH_2)_8CH_3\}$ at the temperature 298.15 K. ———, Values obtained with equation (1) and the parameters of table 3; — — —, Nitta et al.;[14] — — — —, Flory;[15] $\bigcirc$, Grolier et al.;[3] $\triangle$, Awwad and Ibara;[4] $\square$, Pintos et al.;[5] $\bullet$, Ilic et al.[6]

there was a marked difference between the error for the ethanoate-containing mixture: $|0.03 \cdot H_m^E|$, and the errors for the remaining mixtures: $|0.20 \cdot H_m^E|$. A similar finding was reported earlier for UNIFAC-1 by Ortega et al.[13] The equation of Nitta et al.[14] yielded a mean estimation error $< |0.08 \cdot H_m^E|$, while the mean error for the H_m^E predictions obtained using Flory's[15] theory was $|0.10 \cdot H_m^E|$. Figure 1 (a to f) also furnishes qualitative information on each of the methyl esters.

Only two of the preceding theories, those of Nitta et al. model and of Flory, were applied to calculate the excess volumes. Figure 2 represents the six mixtures together with the results obtained by applying the theories and the literature values. The V_m^E estimates obtained using both the theories of Nitta et al. model and of Flory were higher than the experimental values, and the mean errors were $|0.13 \cdot V_m^E|$ for the former and $|0.32 \cdot V_m^E|$ for the latter for all six of the mixtures combined.

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