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ENTHALPIES OF MIXING AT 298.15 K OF A METHYL ALKANOATE (FROM ACETATE TO PENTANOATE) WITH *n*-ALKANES (*n*-TRIDECANE AND *n*-PENTADECANE)

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ABSTRACT

Excess molar enthalpies h^E have been measured for the binary liquid mixtures of four methyl alkanoates (acetate, propanoate, butanoate and pentanoate) with two *n*-alkanes (*n*-tridecane and *n*-pentadecane) at 298.15 K, using an isothermal microcalorimeter. All the mixtures studied were endothermic, the h^E values for a given *n*-alkane decreasing with lengthening of the aliphatic chain of the methyl ester. By contrast, the values of h^E increased quasi-regularly as the number of carbon atoms in the *n*-alkane increased.

INTRODUCTION

The present paper is one of a series dealing with mixtures of esters and various organic solvents such as *n*-alkanes, *n*-alcohols and 1-chloroalkanes, the aim of which is to collect information on the mixing process for binary systems in which one of the components is an ester. In the interest of conducting the investigations systematically, the series started off with binary systems consisting of esters with inert components such as *n*-alkanes, varying the size of the aliphatic chain of both the ester and the *n*-alkane. An earlier paper [1] presented excess molar enthalpies h^E for a number of binary mixtures of methyl esters and *n*-nonane. In the present study, the excess molar enthalpies of eight binary systems $\{C_mH_{2m+1}COOCH_3$ $(m = 1, 2, 3, 4) + C_nH_{2n+2}$ $(n = 13, 15)\}$ were determined at 298.15 K, in order to provide a better basis for analyzing the behavior of such mixtures.

EXPERIMENTAL

All the chemicals employed were degassed ultrasonically for several hours, dried on a molecular sieve (Union Carbide Type 4A, Fluka), and then used without any additional purification. The properties of the methyl esters

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(Fluka) were as described in a previous paper [1]. The physical properties of the *n*-alkanes were also determined at 298.15 K in order to check the purity of the compounds. The results were: *n*-tridecane (Fluka), purity > 99.5 mol%, $\rho = 752.65$, 752.71 kg m^{-3} [2], $n_D = 1.4237$, 1.42346 [2]; *n*-pentade-

TABLE 1

Molar excess enthalpies h^E for methyl alkanoate+(*n*-tridecane and *n*-pentadecane) mixtures at 298.15 K

x_1	h^E (J mol^{-1})	x_1	h^E (J mol^{-1})	x_1	h^E (J mol^{-1})
x_1 Methyl acetate + x_2 *n*-tridecane					
0.1117	822.9	0.6250	2280.7	0.8957	1174.6
0.2392	1545.5	0.6609	2220.8	0.9242	943.5
0.3655	2040.6	0.7007	2122.4	0.9549	645.1
0.4549	2236.5	0.7750	1848.0	0.9785	339.3
0.5293	2310.8	0.8190	1631.5		
0.5672	2316.2	0.8597	1411.1		
x_1 Methyl propanoate + x_2 *n*-tridecane					
0.0828	475.8	0.6095	1856.3	0.8492	1083.2
0.1850	976.7	0.6371	1812.7	0.8856	891.1
0.2917	1395.7	0.6670	1760.5	0.9203	673.0
0.3720	1644.9	0.7000	1672.9	0.9517	432.5
0.4488	1824.1	0.7352	1568.0	0.9783	217.8
0.5191	1892.1	0.7707	1440.7		
0.5745	1888.4	0.8103	1280.3		
x_1 Methyl butanoate + x_2 *n*-tridecane					
0.0744	370.7	0.5266	1546.4	0.8320	961.9
0.1650	741.9	0.5712	1537.6	0.8741	777.6
0.2625	1079.2	0.6456	1458.4	0.9145	569.2
0.3359	1290.4	0.7173	1310.5	0.9511	348.3
0.4104	1437.3	0.7445	1247.5	0.9826	133.9
0.4696	1510.7	0.7884	1119.1		
x_1 Methyl pentanoate + x_2 *n*-tridecane					
0.0650	295.1	0.5018	1284.1	0.7881	925.0
0.1413	577.6	0.5450	1288.3	0.8320	786.9
0.2280	852.9	0.6152	1246.6	0.8754	626.0
0.3158	1066.4	0.6539	1204.7	0.9145	457.3
0.3835	1176.7	0.6980	1135.0	0.9488	290.3
0.4489	1255.8	0.7429	1042.7	0.9764	141.6
x_1 Methyl acetate + x_2 *n*-pentadecane					
0.1088	815.0	0.6207	2401.5	0.8344	1649.2
0.2285	1510.9	0.6871	2280.2	0.8688	1422.8
0.3507	2050.1	0.7130	2204.0	0.9015	1188.6
0.4387	2288.6	0.7404	2098.2	0.9323	921.3
0.5165	2408.2	0.7697	1978.3	0.9599	618.1
0.5762	2428.3	0.8016	1847.1	0.9837	267.3

(continued)

TABLE 1 (continued)

x_1	h^E (J mol^{-1})	x_1	h^E (J mol^{-1})	x_1	h^E (J mol^{-1})
x_1 Methyl propanoate + x_2 *n*-pentadecane					
0.1315	790.2	0.5779	1980.3	0.8632	1149.8
0.2337	1260.9	0.6504	1896.3	0.9127	831.2
0.3371	1640.4	0.7274	1710.8	0.9509	503.7
0.4153	1852.9	0.7565	1621.9	0.9811	217.0
0.4908	1965.9	0.7864	1511.5		
0.5383	1988.2	0.8191	1376.3		
x_1 Methyl butanoate + x_2 *n*-pentadecane					
0.0846	453.0	0.5299	1638.1	0.7931	1216.5
0.1834	873.1	0.5731	1635.5	0.8384	1041.9
0.2618	1160.4	0.6091	1611.1	0.8824	830.5
0.3457	1392.3	0.6749	1521.3	0.9246	583.0
0.4121	1536.8	0.7103	1456.6	0.9650	305.2
0.4778	1610.9	0.7491	1352.6		
x_1 Methyl pentanoate + x_2 *n*-pentadecane					
0.0783	349.3	0.4895	1360.1	0.7790	1063.9
0.1671	667.5	0.5340	1376.7	0.8229	923.5
0.2385	895.9	0.6001	1360.6	0.8648	761.7
0.3179	1094.0	0.6553	1324.0	0.9051	576.9
0.3823	1221.9	0.6933	1264.4	0.9416	376.4
0.4359	1296.5	0.7358	1178.5	0.9736	183.6

cane (Aldrich), purity > 99 mol%, $\rho = 765.05$, 764.88 kg m^{-3} [3], $n_D =$ 1.4298, 1.42979 [3].

Mixing enthalpies were measured using a Calvet MS70 microcalorimeter (Setaram), the operating procedure for which was as described previously [4]. The estimated error in the determinations of the concentration of the methyl ester was less than 5×10^{-4}; taking the mixture of *n*-hexane + cyclohexane [5] as a standard system, the estimated error for the h^E values was around 1%.

RESULTS AND DISCUSSION

Table 1 presents the experimental h^E values for the eight mixtures $\{x_1\ C_mH_{2m+1}COOCH_3 + x_2\ C_nH_{2n+2};\ m = 1, 2, 3, 4;\ n = 13, 15\}$. Figure 1 shows the h^E data points in relation to the values of x_1, the mole fraction of the methyl ester, together with the plots of the curves fitted to the experimental data. The curves were obtained using the polynomial equation

$$h^E(\text{in J mol}^{-1}) = x_1 x_2 \sum_{i=0} A_i \left[x_1/(x_1 + kx_2)\right]^i \qquad (1)$$

TABLE 2

Coefficients A_i in eqn. (1) and standard deviations $s(h^E)$ for methyl alkanoate+(n-tridecane and n-pentadecane) mixtures at 298.15 K

System	k	A_0	A_1	A_2	A_3	$s(h^E)$
x_1 Methyl acetate + x_2 n-tridecane	5.031	8028.0	8348.7	−9756.8	12293.5	8.2
x_1 Methyl propanoate + x_2 n-tridecane	3.099	5798.9	10717.3	−18698.0	13204.6	8.2
x_1 Methyl butanoate + x_2 n-tridecane	2.367	4991.7	5903.2	−8945.3	6282.6	7.2
x_1 Methyl pentanoate + x_2 n-tridecane	2.229	4699.2	1364.1			3.3
x_1 Methyl acetate + x_2 n-pentadecane	4.787	7996.4	11172.1	−14054.0	14421.0	9.5
x_1 Methyl propanoate + x_2 n-pentadecane	2.376	6391.6	7208.8	−10193.4	8939.1	8.9
x_1 Methyl butanoate + x_2 n-pentadecane	2.891	5556.7	4729.0	−5267.5	4688.2	5.1
x_1 Methyl pentanoate + x_2 n-pentadecane	1.933	4574.3	2532.8			5.0

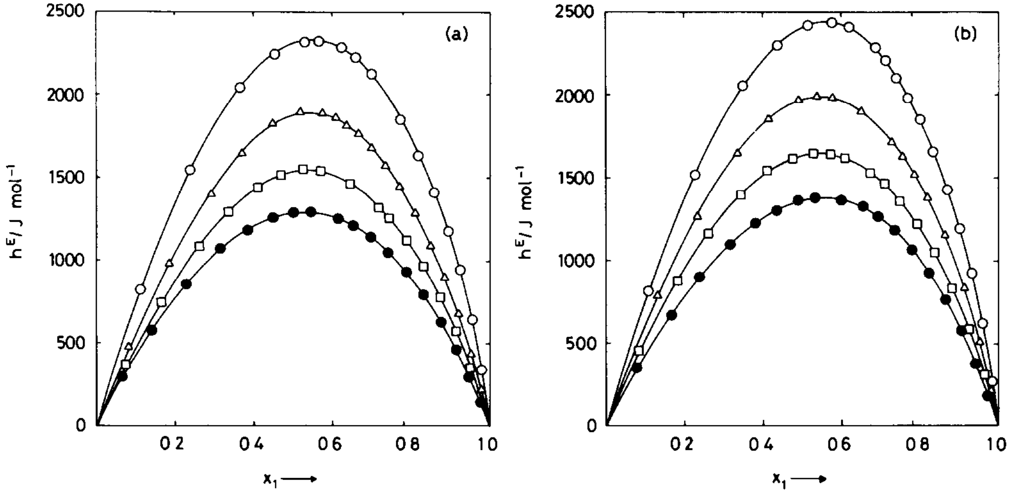

Fig. 1. Experimental and calculated excess molar enthalpies h^E of: (a) $\{x_1\ C_mH_{2m+1}COOCH_3 + x_2\ C_{13}H_{28}\}$ and (b) $\{x_1\ C_mH_{2m+1}COOCH_3 + x_2\ C_{15}H_{32}\}$. ○, $m = 1$; △, $m = 2$; □, $m = 3$; ●, $m = 4$.

The values of the parameters A_i and k were calculated for each system by an unweighted least-squares method, and are set out, along with the standard deviations $s(h^E)$, in Table 2. The most appropriate degree of the polynomial in eqn. (1) was chosen for each system on the basis of a statistical criterion (F-test) [6].

All of the mixtures were endothermic, with positive excess enthalpies. The values of the mixing enthalpies for the systems and the values for n-nonane published in an earlier paper [1] presented a quasi-linear distribution at $x = 0.5$, and rose as the chain length of the n-alkane increased. This was probably the well-known "size-effect". For the ester, on the other hand, the h^E values at $x = 0.5$ decreased as the length of the aliphatic chain of the methyl alkanoate increased. This is in accordance with the findings of other workers [7,8], as the behavior to be expected for mixtures of an ester with an n-alkane, and would appear to be caused by the polarity of the ester group, which weakens as the chain length grows. This effect is intensified in mixtures of esters with n-alkanes by the fact that the molecules of the n-alkane become interposed between those of the ester, reducing the contact between the molecules of the ester; and this is the basic cause of the endothermism of these systems.

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