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EXCESS MOLAR ENTHALPIES OF METHYL ALKANOATES + *n*-NONANE AT 298.15 K

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ABSTRACT

Microcalorimetric measurements of excess enthalpies were carried out over the whole concentration range for mixtures of nine methyl alkanoates (from acetate to decanoate) with *n*-nonane at 298.15 K. From these data, information could be obtained about the interactions between both chemical species. All show positive excess molar enthalpies which decrease with increasing length of the aliphatic chain of the methyl alkanoate.

INTRODUCTION

The thermodynamic properties of ester + hydrocarbon systems have been the subject of extensive investigation in an attempt to examine the interactions between the chemical species making up such systems. Specifically, different magnitudes have been studied for methyl alkanoate + *n*-alkane systems by Grolier et al. [1], Dusart et al. [2,3], and, more recently, by Pintos et al. [4] and De Soria et al. [5].

The present authors have published a series of papers on systems composed of a methyl alkanoate together with an *n*-alkanol [6] or a 1-chloroalkane [7] as the second component, but they nevertheless feel that there is merit in furnishing new experimental h^E data for methyl alkanoate + *n*-alkane systems with increasing size of the aliphatic chain of the alkanoate. They therefore present here h^E data at 298.15 K for nine binary systems $[x_1C_mH_{2m+1}CO_2CH_3$ ($m = 1$ to 9) + $x_2C_9H_{20}]$ intended to assist in verification of the assessments of such binary mixtures made to date. No data for such systems were found in the literature searched.

EXPERIMENTAL

All the chemicals used in this study were from Fluka AG. The nonane, purity > 99 mol%, showed physical properties (n_D and ρ) that were in good

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TABLE 1

Physical properties, ρ and n_D, of methyl alkanoates at 298.15 K

Compound	ρ (kg m^{-3})		n_D	
	Experimental	Literature	Experimental	Literature
Methyl acetate	927.07	927.9 [8] 926.79 [4] 927.30 [3]	1.3589	1.3589 [8]
Methyl propanoate	908.86	909.0 [9] 909.01 [4] 909.32 [3]	1.3745	1.3742 [9]
Methyl butanoate	892.61	892.6 [9] 892.17 [4] 892.60 [3]	1.3849	1.3847 [9]
Methyl pentanoate	884.50	884.66 [4] 885.22 [3]	1.3947	–
Methyl hexanoate	879.44	879.86 [3]	1.4029	–
Methyl heptanoate	875.32	–	1.4094	–
Methyl octanoate	872.38	872.30 [4]	1.4148	–
Methyl nonanoate	870.12	–	1.4195	–
Methyl decanoate	868.18	–	1.4232	–

agreement with those reported in the literature [8]. Data on the properties of the methyl alkanoates do not abound in the literature, and Table 1 therefore shows the experimental density and refractive index values together with those compiled from the sources consulted. All component liquids were employed without further purification; however, the mixtures of liquids were degassed ultrasonically and then dried with a molecular sieve (Union Carbide type 4A) from Fluka AG before experimental measurements were taken.

The excess molar enthalpies h^E were determined with a Calvet MS-70 microcalorimeter, from Setaram. The operating procedures were described in a previous paper [10]. The errors in the h^E determination and in the molar fraction x were estimated to be less than 1% and 5×10^{-4}, respectively.

RESULTS AND DISCUSSION

The experimental h^E values for the nine binary mixtures $[x_1C_mH_{2m+1}CO_2CH_3$ ($m = 1$ to 9) $+ x_2C_9H_{20}]$ are shown in Table 2. Correlations were established using the following polynomial equation

$$h^E \text{ (J mol}^{-1}) = x_1x_2\sum_i A_i[x_1/(x_1 + kx_2)]^i \quad (1)$$

The A_i coefficients were determined by a least squares method, by varying the value of k until the minimum standard deviation, $s(h^E)$, was achieved with respect to the experimental values. Table 3 gives the coeffi-

TABLE 2

Molar excess enthalpies h^E for methyl alkanoate + *n*-nonane 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})
Methyl acetate (1) + *n*-nonane (2)					
0.1360	850.7	0.5753	2016.2	0.8129	1370.8
0.2689	1475.5	0.6205	1962.7	0.8538	1157.8
0.3594	1776.6	0.6415	1927.3	0.8951	902.6
0.4310	1936.7	0.6830	1840.9	0.9353	609.1
0.4895	2010.7	0.7285	1714.4	0.9709	301.8
0.5368	2024.9	0.7698	1564.9		
Methyl propanoate (1) + *n*-nonane (2)					
0.1112	574.7	0.5417	1640.2	0.7745	1176.2
0.2204	1025.6	0.5786	1605.9	0.8212	1008.5
0.3083	1335.8	0.6091	1563.3	0.8673	801.4
0.3765	1501.5	0.6601	1480.3	0.9214	521.9
0.4437	1608.9	0.7022	1386.0	0.9633	268.6
0.4970	1646.5	0.7315	1301.8		
Methyl butanoate (1) + *n*-nonane (2)					
0.0952	442.3	0.4989	1316.4	0.7522	978.8
0.1976	786.6	0.5372	1310.8	0.8028	834.3
0.2930	1057.8	0.5703	1295.4	0.8568	651.5
0.3553	1187.7	0.5976	1270.7	0.9076	447.7
0.4072	1258.9	0.6545	1188.1	0.9567	222.5
0.4522	1294.9	0.6997	1104.6		
Methyl pentanoate (1) + *n*-nonane (2)					
0.0806	330.9	0.5073	1102.3	0.7811	735.4
0.1715	620.0	0.5464	1092.0	0.8380	582.4
0.2599	845.2	0.6063	1040.2	0.8962	399.3
0.3421	993.4	0.6436	998.3	0.9499	205.7
0.4077	1068.2	0.6870	935.6		
0.4621	1098.4	0.7309	848.1		
Methyl hexanoate (1) + *n*-nonane (2)					
0.0809	307.2	0.4763	934.3	0.7215	735.0
0.1648	539.5	0.5189	933.7	0.7703	640.8
0.2430	709.4	0.5555	915.0	0.8258	512.6
0.3181	821.2	0.6010	894.4	0.8904	341.1
0.3802	889.7	0.6376	856.3	0.9525	159.8
0.4319	922.6	0.6795	801.4		
Methyl heptanoate (1) + *n*-nonane (2)					
0.0684	246.5	0.4466	843.4	0.6989	678.9
0.1438	446.2	0.4844	843.3	0.7496	596.6
0.2188	611.0	0.5165	834.6	0.8073	482.3
0.2918	730.6	0.5676	818.7	0.8747	331.4
0.3528	799.3	0.6059	788.8	0.9410	172.5
0.4030	831.0	0.6484	745.3		

TABLE 2 (continued)

x_1	h^E (J mol^{-1})	x_1	h^E (J mol^{-1})	x_1	h^E (J mol^{-1})
Methyl octanoate (1) + *n*-nonane (2)					
0.0647	217.8	0.4351	763.2	0.7250	553.6
0.1345	400.0	0.5000	754.7	0.7951	437.9
0.2072	541.3	0.5317	745.4	0.8663	299.7
0.2790	648.3	0.5717	721.9	0.9374	155.7
0.3389	709.3	0.6146	686.8		
0.3950	745.6	0.6651	633.5		
Methyl nonanoate (1) + *n*-nonane (2)					
0.0550	181.3	0.4203	698.4	0.6544	566.6
0.1216	350.8	0.4694	699.4	0.7155	493.1
0.1889	490.1	0.4973	692.9	0.7871	390.9
0.2555	588.6	0.5305	679.6	0.8584	269.0
0.3198	653.3	0.5632	658.0	0.9331	134.1
0.3732	683.8	0.6057	617.7		
Methyl decanoate (1) + *n*-nonane (2)					
0.0545	174.9	0.4213	657.0	0.7017	469.3
0.1205	326.6	0.4625	654.5	0.7686	377.0
0.1869	454.6	0.4950	644.7	0.8481	254.1
0.2526	550.8	0.5411	814.7	0.9291	127.6
0.3137	613.7	0.5858	580.1		
0.3714	649.8	0.6388	531.8		

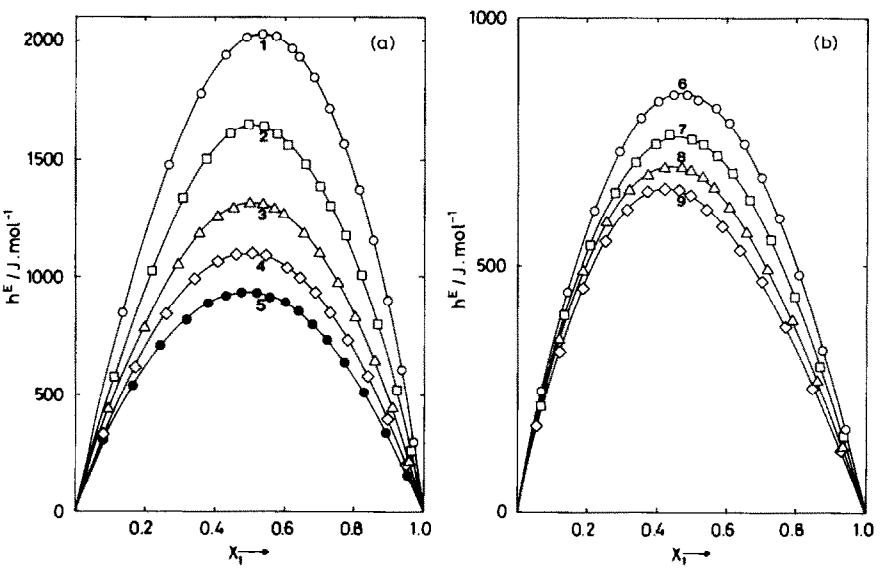

Fig. 1. Molar excess enthalpies h^E for $x_1C_mH_{2m+1}CO_2CH_3$ ($m = 1$ to 9) + $x_2C_9H_{20}$. Labels indicate m. Solid lines represent eqn. (1) with the coefficients of Table 3.

TABLE 3

Coefficients A_i in eqn. (1) and standard deviation $s(h^E)$ at 298.15 K for methyl alkanoates + *n*-nonane

Mixture	k	A_0	A_1	A_2	A_3	A_4	$s(h^E)$ (J mol^{-1})
Methyl acetate (1) + *n*-nonane (2)	2.630	6897.8	6004.0	−8433.3	6837.9	–	3.0
Methyl propanoate (1) + *n*-nonane (2)	0.674	6783.1	−12828.7	53670.6	−77268.2	37452.9	4.4
Methyl butanoate (1) + *n*-nonane (2)	0.512	6398.6	−12856.4	39033.7	−46041.6	18897.8	2.8
Methyl pentanoate (1) + *n*-nonane (2)	0.752	4320.7	481.7	−597.9	–	–	3.9
Methyl hexanoate (1) + *n*-nonane (2)	0.650	4432.1	−3201.5	5337.1	−3187.0	–	2.6
Methyl heptanoate (1) + *n*-nonane (2)	0.218	4705.1	−5140.8	8302.0	−4882.6	–	3.6
Methyl octanoate (1) + *n*-nonane (2)	0.354	4039.1	−3289.8	5089.8	−3382.6	–	2.8
Methyl nonanoate (1) + *n*-nonane (2)	0.342	3785.0	−2567.9	3944.9	−3152.5	–	2.7
Methyl decanoate (1) + *n*-nonane (2)	0.186	4726.4	−8673.6	15293.4	−9555.2	–	3.2

cients and the corresponding standard deviations for each system; these values were used to fit the curves shown in Fig. 1.

Figure 1 clearly illustrates the qualitative and quantitative features of the behaviour of the systems considered. All the mixtures showed endothermic behaviour over the entire range of concentrations, and the h^E values diminished as the alkyl moiety of the methyl alkanoate increased in length, thereby confirming once again the characteristic behaviour of alkyl alkanoates mixed with *n*-alkanes as well as with other components, such as *n*-alkanols and 1-chloroalkanes. Such behaviour also occurs when other thermodynamic quantities, e.g. v^E and g^E, are studied.

Summing up all the positive and negative contributions taking part in the mixing process for the components considered here, as discussed in an earlier paper [11], yields positive h^E values, indicative of the endothermic effect of such mixtures.

The presence of an *n*-alkane in the binary systems studied here is another important aspect of the investigation, and additional experimental data will be presented in future papers in order to make the analysis more comprehensive by encompassing a large number of different components.

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