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Experimental and predicted mixing enthalpies for several methyl *n*-alkanoates with *n*-pentane at 298.15 K. Application of the UNIFAC model

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Abstract

Mixing enthalpy values for nine binary systems consisting of methyl esters (from ethanoate to *n*-decanoate) and *n*-pentane measured at 298.15 K and normal atmospheric pressure using a Calvet microcalorimeter are reported. The experimental results showed that the h^E values are positive over the entire range of concentrations and that they decrease in a regular manner as the ester chain-length increases. The experimental values were compared with predictions obtained by applying the UNIFAC model using various options. Mean estimation errors for the nine systems ranged between 7.1% and 25.6%, depending on the individual model case applied.

INTRODUCTION

This paper continues our investigations into the thermodynamic properties of binary systems composed of methyl esters and *n*-alkanes. Previous papers have presented mixing enthalpy h^E values for fourteen methyl *n*-alkanoates (from ethanoate to *n*-pentadecanoate) and *n*-alkanes with an odd number of carbon atoms (from *n*-heptane to *n*-pentadecane) [1–5]. Pursuing these same lines, h^E values are reported for nine binary mixtures, C_uH_{2u+1} $COOCH_3$ $(u = 1–9) + n\text{-}C_5H_{12}$, measured at 298.15 K and normal atmospheric pressure. The literature consulted disclosed mixing enthalpy values for the methyl ethanoate + *n*-pentane system only [6]; these have been used for purposes of comparison.

Systematization of the investigation is important in order to be able to determine the interaction energies between the components employed and, thus, to ensure a more rational examination of the theoretical models used to predict the behavior of mixtures. In recent years group contribution models have gained importance in estimating various mixing properties in chemical engineering thermodynamics. The UNIFAC model, put forward by Fredenslund et al. [7] for use with VLE data, is one of the most important. However, it transpired that the interaction parameters required to reproduce mixing enthalpy values were different from those used in the original model. Rupp et al. [8] subsequently obtained good results in the prediction of h^E values applying ideas set forth by Nagata and Ohta [9] (UNIFAC-1). In an earlier paper [5] more extensive input data were used to calculate revised parameter values for the alkane/ester interactions, modifying those published by Rupp et al. [8]; these modified parameter values have been used again in this study in order to evaluate their suitability. The version of the UNIFAC model of Larsen et al. [10] (UNIFAC-2) has also been applied for comparison purposes, with a view to verifying the effectiveness of this version of the UNIFAC group contribution model.

EXPERIMENTAL

Both the methyl esters and *n*-pentane were from Fluka and were of the highest commercial grade. Therefore, the only treatments applied before use were degassing followed by drying on a molecular sieve (ref. 69828, Fluka). The physical properties of the methyl *n*-alkanoates as determined at 298.15 K showed rather good agreement with those reported in previous papers [1,3]. The refractive index and density of the *n*-pentane measured at the working temperature were: $n_D = 1.3547$, 1.35472 [11,12]; $\rho(\text{kg m}^{-3}) =$ 621.31, 621.39 [11], 612.2 [12].

The h^E values were determined in a Calvet microcalorimeter with automatic integration of the electrical signal. The device was calibrated based on the Joule effect by applying different electric current values from a direct current generator. The precision of the equipment was validated by measuring the h^E for a standard mixture of *n*-hexane + cyclohexane. The differences between our data and the curve provided by McGlashan and Stoeckli [13] gave an estimated mean error of 0.7%; the differences with respect to the more recent values published by Yan et al. [14] were slightly higher, in the order of 0.9%. Analysis of the errors between the experimental and calculated values yielded an error of 1% in the final values for h^E and an error of $\pm 5 \times 10^{-4}$ in the mixture concentrations values.

TREATMENT OF RESULTS

Table 1 gives the experimental mixing enthalpy (h^E) values measured at 298.15 K for the nine binary systems $x_1C_uH_{2u+1}COOCH_3(u = 1\text{–}9) + x_2n\text{-}C_5H_{12}$. These data were correlated using the equation

$$h^E(\text{J mol}^{-1}) = x_1x_2 \sum_{i=0} A_i[x_1/(x_1 + kx_2)]^i \qquad (1)$$

TABLE 1

Excess molar enthalpies h^E for $x_1 n\text{-}C_uH_{2u+1}COOCH_3$ ($u = 1\text{–}9$) + $x_2 n\text{-}C_5H_{12}$ 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})
$x_1CH_3COOCH_3 + x_2 n\text{-}C_5H_{12}$					
0.0534	372.0	0.4663	1518.5	0.7453	1072.8
0.1151	678.7	0.5118	1520.9	0.7843	944.6
0.1803	952.0	0.5787	1476.7	0.8259	789.7
0.2431	1162.3	0.6005	1443.4	0.8642	625.9
0.3043	1315.6	0.6321	1377.1	0.9009	484.7
0.3628	1424.7	0.6680	1300.3	0.9380	296.3
0.4170	1490.4	0.7056	1208.9	0.9734	125.3
$x_1C_2H_5COOCH_3 + x_2 n\text{-}C_5H_{12}$					
0.0480	280.7	0.4221	1193.8	0.6932	936.5
0.1010	522.3	0.4673	1201.6	0.7381	824.6
0.1528	698.6	0.5122	1189.7	0.7827	720.7
0.2092	869.0	0.5407	1163.7	0.8276	570.3
0.2665	1004.9	0.5741	1123.9	0.8793	405.7
0.3208	1099.8	0.6114	1075.6	0.9218	271.2
0.3734	1163.3	0.6548	1002.3	0.9609	130.8
$x_1 n\text{-}C_3H_7COOCH_3 + x_2 n\text{-}C_5H_{12}$					
0.0909	412.9	0.4218	992.2	0.7042	728.4
0.1538	624.1	0.4575	995.0	0.7551	619.1
0.2079	761.3	0.4915	986.0	0.8108	492.3
0.2561	858.7	0.5176	972.6	0.8630	359.1
0.3044	930.6	0.5581	935.4	0.9150	223.1
0.3470	963.0	0.6083	879.7	0.9594	111.4
0.3871	984.2	0.6582	808.0	–	–
$x_1 n\text{-}C_4H_9COOCH_3 + x_2 n\text{-}C_5H_{12}$					
0.0336	155.7	0.3466	824.4	0.7098	604.5
0.0742	314.0	0.4003	845.1	0.7608	510.4
0.1174	453.6	0.4671	839.6	0.8098	412.9
0.1602	574.3	0.5149	825.6	0.8577	308.5
0.2078	664.7	0.5609	785.5	0.9073	209.1
0.2548	738.2	0.6099	737.9	0.9542	108.2
0.3024	792.1	0.6573	688.2	–	–
$x_1 n\text{-}C_5H_{11}COOCH_3 + x_2 n\text{-}C_5H_{12}$					
0.0234	118.3	0.3216	720.8	0.5951	656.5
0.0610	269.0	0.3634	733.8	0.6460	607.2
0.1023	398.3	0.4009	735.5	0.7043	527.3
0.1458	500.0	0.4308	737.7	0.7634	429.8
0.1907	583.6	0.4632	735.6	0.8250	322.0
0.2354	645.9	0.5037	719.5	0.8874	207.8
0.2778	690.5	0.5566	687.5	0.9464	96.6
$x_1 n\text{-}C_6H_{13}COOCH_3 + x_2 n\text{-}C_5H_{12}$					
0.0263	125.7	0.2988	645.1	0.6031	557.3
0.0569	236.3	0.3374	661.0	0.6622	497.0
0.0936	345.9	0.3725	665.2	0.7244	423.6
0.1330	440.5	0.4047	662.4	0.7912	338.5
0.1742	517.0	0.4532	645.9	0.8637	225.5
0.2158	575.6	0.4991	631.4	0.9328	117.3
[illegible]	617.0	0.5471	600.3		–

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_1n-$C_7H_{15}COOCH_3 + x_2n$-C_5H_{12}					
0.0559	219.0	0.3406	588.8	0.6707	434.2
0.0843	302.4	0.3772	591.9	0.7375	363.0
0.1276	404.9	0.4177	588.1	0.8029	287.2
0.1711	483.9	0.4575	572.9	0.8662	195.1
0.2119	531.4	0.5036	559.0	0.9346	96.0
0.2546	564.3	0.5535	531.1	–	–
0.2976	582.0	0.6105	487.9	–	–
x_1n-$C_8H_{17}COOCH_3 + x_2n$-C_5H_{12}					
0.0870	297.6	0.5340	483.5	0.7976	235.5
0.1740	465.7	0.6078	436.5	0.8371	189.8
0.2629	533.2	0.6437	403.3	0.8736	147.7
0.3393	545.8	0.6811	372.2	0.9103	105.6
0.4120	539.1	0.7176	329.6	0.9451	62.9
0.4762	516.2	0.7574	281.2	0.9752	28.3
x_1n-$C_9H_{19}COOCH_3 + x_2n$-C_5H_{12}					
0.0512	187.0	0.2978	504.2	0.6456	341.3
0.0832	285.3	0.3362	507.6	0.7095	283.2
0.1171	357.8	0.3690	511.4	0.7750	217.5
0.1497	410.7	0.4353	487.5	0.8454	151.4
0.1869	454.6	0.4824	459.8	0.9233	80.2
0.2242	483.7	0.5363	430.6	–	–
0.2616	501.1	0.5871	395.1	–	–

The coefficients in the equation were calculated by a method of least-squares. Table 2 lists the optimized values of k and A_i for each system along with the standard deviations with respect to the experimental values

TABLE 2

Values of k and A_i and standard deviations $s(h^E)$ obtained for eqn. (1) for h^E [x_1n-$C_uH_{2u+1}COOCH_3(u=1$–$9) + x_2n$-C_5H_{12}] at 298.15 K

u	k	A_0	A_1	A_2	A_3	$s(h^E)$
1	0.53	8054.9	−9654.9	17164.0	−10673.6	6.8
2	0.44	6805.1	−7523.3	11935.6	−7677.0	5.9
3	1.12	5366.5	−4709.0	4876.2	−2987.3	3.2
4	0.88	5023.4	−5507.2	6240.8	−3591.1	4.2
5	0.78	5278.6	−8812.6	11809.6	−6600.3	2.8
6	0.30	4883.9	−3068.0	–	–	2.7
7	0.24	4887.5	−3277.5	–	–	4.2
8	0.30	4538.7	−3277.9	–	–	6.1
9	0.29	4529.0	−3528.0	–	–	4.0

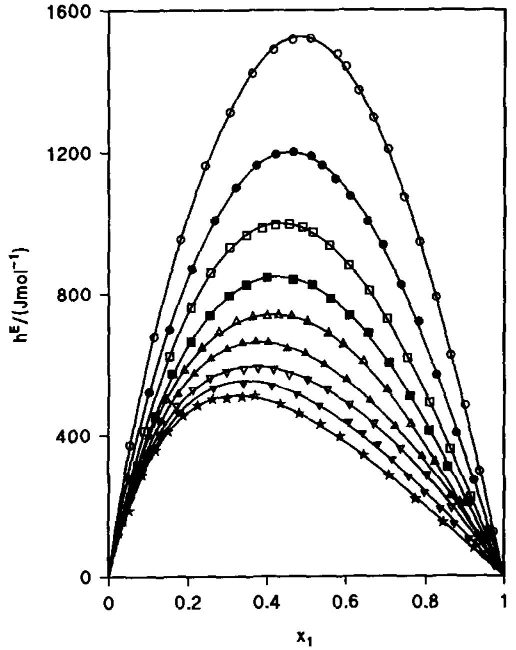

Fig. 1. Experimental excess molar enthalpies at 298.15 K of $x_1 n$-$C_uH_{2u+1}COOCH_3 + x_2 n$-$C_5H_{12}$: ○, $u = 1$; ●, $u = 2$; □, $u = 3$; ■, $u = 4$; △, $u = 5$; ▲, $u = 6$; ▽, $u = 7$; ▼, $u = 8$; ☆, $u = 9$; ———, calculated from eqn. (1) with coefficients from Table 2.

for the fitting function, eqn. (1). The plots in Fig. 1 were prepared using these values and the experimental values in Table 1; the figure also gives the curve for the system methyl ethanoate + *n*-pentane, taken from de Soria et al. [6], which has an estimated mean error of 19.5% and an absolute difference of 115.4 J mol^{-1} at $x_1 = 0.5$. The plots for the nine systems show that the mixing enthalpies decrease in a quasi-regular manner as the chain length of the methyl ester increases, an expected result that confirms again the behavior already described for mixtures of esters and *n*-alkanes.

Different cases of alkane/ester interaction were considered when applying the UNIFAC model. Rupp et al.'s [8] version (UNIFAC-1) differs from the former mainly in the dependence of the interaction parameters on temperature.

Figure 2 depicts the mean errors for each of the nine systems considered. Application of UNIFAC-1 using the parameters for the interaction pair CH_2/COOC suggested by Rupp et al. [8] did not yield good results, with errors larger than 23% except for the ethanoates. This was reported previously by Ortega et al. [5], who attributed this to the fact that the parameters used by Rupp et al. [8] were calculated from a small data base in which alkyl ethanoates predominated; therefore the following new parameter values were proposed [5]: $CH_2/CH_2COO = 54.89$ and

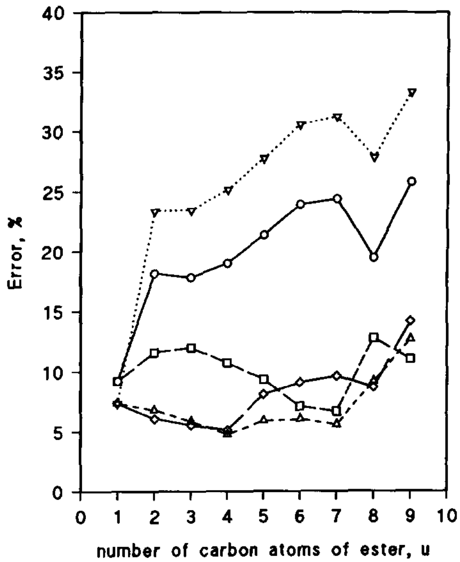

Fig. 2. Error percents obtained using different forms of the UNIFAC model as a function of the number of carbon atoms *u* of methyl ester. Rupp et al. [8]: ▽, $-CH_2COO-$; △, $-COOCH_3$. Larsen et al. [10]: ○, $-CH_2COO-$; □, $-COOCH_3$. Ortega et al. [5]: ◇, $-CH_2COO-$.

$CH_2COO/CH_2 = 86.06$. Applying these new values lowered the overall mean error for the nine systems from 25.6% (using parameters in ref. 8) to 8.2%. The UNIFAC-2 model yielded an overall mean error of 18.8% for all the systems as a whole, with the error increasing slightly with methyl ester chain length (Fig. 2). Nevertheless, in both the UNIFAC-1 and UNIFAC-2 models the original parameter values yielded good predictions for mixtures containing alkyl ethanoates, and were thus appropriate for the methyl *n*-alkanoates, considering the principal group to be $-COOCH_3$ rather than $-CH_2COO-$. Applying this consideration of the principal group produced a quite acceptable estimate for the set of systems overall, with a mean error of 7.1% for the UNIFAC-1 model and 10% for the UNIFAC-2 model. Of course, the basis for this consideration is practical rather than scientific, and it cannot be applied to other esters, $R_1-COO-R_2$ in which both R_1 and R_2 contain more than one carbon atom.

CONCLUSIONS

Experimental h^E values at 298.15 K for binary mixtures composed of nine methyl esters and *n*-pentane are presented. The physicochemical behavior of these systems was analogous to that of other mixtures of (esters + *n*-alkanes) and brought about a quasi-exponential reduction in mixing enthalpy values as the length of aliphatic chain R_1 in R_1COOCH_3

increased. The UNIFAC group contribution model was applied to predict the h^E values, and revised parameters for the ester + alkane interaction were also employed. The best results were obtained when the model was applied separately to the alkyl ethanoates and the other esters.

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