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Calorimetric measurement of molar excess enthalpies of dilute solutions of ethylbenzene + higher *n*-alkanes

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Abstract

Flow calorimetry has been used to measure the excess enthalpies (heats of mixing) of dilute solutions of higher *n*-alkanes (hexadecane to pentacosane) in ethylbenzene. The results show that at constant temperature and composition, h^E increases with the number of carbon atoms in the *n*-alkane molecule. Also, for each alkane, h^E decreases with increasing temperature, at constant composition.

A simple analytical expression is used to represent the variation of h^E with carbon number n, composition x, and temperature T in the domain ($16 \leq n \leq 25$; $x \leq 0.15$; $298.15 \leq T \leq 330.00$). © 1997 Elsevier Science B.V.

Keywords: Excess thermodynamic properties; *n*-alkanes; Solvent; Crystallization; Wax; Petroleum

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1. Introduction

Normal paraffin hydrocarbons, with chain lengths ranging from 18 to 24 carbon atoms, are the major constituents of the solid deposits from some petroleum products (especially those refined from waxy crudes) at low temperatures. Wax precipitation is a source of nuisance both to refiners and consumers of finished products; the former have sought a number of solutions including dewaxing and the addition of flow improvers. But such solutions are yet unsatisfactory, as they are either expensive, or may lead to defects in fuel properties. Also, the effectiveness of fuel improvers is now known to depend on its concentration and on the concentration and distribution of normal paraffins in the fuel [1,2]. New, acceptable solutions may come from a study of these suspected compounds.

Thermodynamic investigations of the pure *n*-paraffins, of their mutual mixtures, and of their mixtures in organic solvents, have been the subject of continued research over the last decades [3–14]. But, before a proper appreciation of the complicated wax mixtures present in oil can be hoped for, it is necessary to examine simple systems. This work is, accordingly, one of a series of studies currently underway in this laboratory on the thermodynamic and structural properties of these organic substances [15], and their mixtures [16–22].

Attempts to model solution behaviour are generally centred around the molar excess Gibbs energy, g^E, as a function of mole fraction x, and temperature T [3,6–

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8,14]. But these models fail to correlate or to predict solution behaviours that depend on derivatives of g^E, such as the molar excess enthalpy, h^E. This failure is sometimes (erroneously?) attributed to the so-called Patterson effect [6]. It is however advantageous to study solution behaviour by measuring the derivative excess properties directly. This avoids the inherent loss of precision incurred upon the differentiation of data. On the other hand, integration may enhance precision [3].

In the present work, we report the results of calorimetric measurements of the excess enthalpies (heats of mixing) of ethylbenzene + n-alkanes having between 16 and 25 carbon atoms in their aliphatic chains, for concentrations (mole fractions of n-alkanes) less than 0.16. (The relative proportions of n-paraffins in finished products are less than 10 wt% [23].) Ethylbenzene, chosen as solvent, has the advantage of having an aromatic ring and a short aliphatic side-chain, thus representing on a miniature scale, the petroleum solvent. We have also studied the temperature-dependence of h^E. In the domains of temperature and concentration, all results are fitted to an analytical expression of $h^E(n,x,T)$.

2. Experimental

2.1. Apparatus and procedure

We have used a SETARAM C80D flow calorimeter previously described by Aoulmi [13]. For optimum results, the procedure was modified such that the reference cell did not contain pure solvent, but a dilute solution (concentration x_1) of solute in solvent. The measured quantity ΔQ, permits the determination of the molar excess enthalpy $h^E(x_2)$, of the solution in the experimental cell (concentration x_2 ($x_2 > x_1$)) by the equation:

$$h^E(x_2) = \frac{(n_1 + n_{s1})}{(n_2 + n_{s2})} h^E(x_1) + \frac{\Delta Q}{n_2 + n_{s2}}$$

where n_1, n_2, n_{s1}, n_{s2} are the numbers of moles of paraffin in the reference cell, of paraffin in the experimental cell, of the solvent in the reference cell and of the solvent in the measuring cell, respectively. ΔQ is the integral heat change registered upon mixing. With this procedure, any individual measurement was more reproducible and had an accuracy better than 5 J mol^{-1}. The accuracy of temperature measurement was ±0.05 K.

2.2. Materials

Ethylbenzene was purchased from Aldrich (anhydrous, HPLC grade, 99.8%). n-Hexadecane (anhydrous sure/seal quality) was also bought from Adrich with a purity grade of 99+%. n-Octadecane (Fluka "puriss"), n-nonadecane, n-eïcosane, n-heneïcosane, n-docosane, n-tricosane, n-tetracosane, and n-pentacosane (Aldrich, 99%) were checked by gas chromatography to have a purity of minimum 99%. They were used as purchased. The relative error in composition was less than 1%.

3. Results

Experimental values of molar excess enthalpies are given in Table 1. In all the binaries, x is the mole fraction of the paraffin, and δ is the relative deviation defined by:

$$\delta = \frac{h^E_{cal} - h^E_{expt}}{h^E_{expt}}$$

where h^E_{expt} is the experimental value measured and h^E_{cal} is the corresponding value calculated from the analytical expression given at the end of this section.

3.1. Comparison with existing literature h^E data

No h^E data on ethylbenzene + n-octadecane or higher alkanes have been found in the literature. However, Arenosa et al. (4) measured h^E for ethylbenzene + n-hexadecane at 298.15 K. We decided to repeat their measurements in our composition domain. The comparison of our results with theirs is shown in Fig. 1. Our experimental results are in very good agreement with the literature values.

3.2. Temperature-dependence of h^E

The negative values of C^E_p reported by Matilla et al. [8] suggest that h^E will decrease with increasing temperature, but no precise measurement of this variation has been carried out. For each of the alkanes, we

Table 1
Molar excess enthalpies of *n*-alkanes in ethylbenzene

x[a]	h^E (J mol^{-1})	δ[b]
n-Hexadecane		
T = 298.15 K		
0.0029	13.7	0.05
0.005	23	0.07
0.0096	50	−0.06
0.0306	148	−0.04
0.05	223	−0.01
0.0526	233	−0.01
0.079	320	0.01
0.08	320	0.02
0.1	393	−0.01
0.123	464	−0.04
0.151	525	−0.03
T = 311.55 K		
0.005	23	−0.04
0.0502	201	0.01
0.1029	358	0.03
0.1535	481	0.02
T = 330.00 K		
0.0213	76	−0.05
0.0584	188	0.01
0.075	234	0.01
0.1017	299	0.03
0.125	360	0.02
0.1499	415	0.01
n-Octadecane		
T = 303.15 K		
0.032	155	0.03
0.068	302	0.02
0.095	394	0.02
0.125	474	0.02
0.149	531	0.00
T = 330.00 K		
0.0294	117	−0.01
0.0538	200	0.01
0.073	262	0.01
0.0961	332	0.00
0.1141	378	0.00
0.135	428	−0.01
0.1565	474	−0.01
n-Nonadecane		
T = 311.45 K		
0.0289	141	0.04
0.0498	240	0.00
0.0746	335	0.00
0.0999	415	0.00
0.1234	477	0.00
0.1374	510	0.00
T = 330.00 K		
0.0268	115	−0.01
0.0518	210	−0.01
0.0778	293	0.01
0.1044	371	0.00
0.1249	444	−0.05
0.1479	487	−0.04
n-Eicosane		
T = 313.02 K		
0.0361	192	−0.01
0.051	255	0.01
0.0739	336	0.01
0.1012	428	0.03
0.1339	503	0.02
0.1509	545	0.01
T = 330.00 K		
0.0201	90.6	0.03
0.0351	159	−0.02
0.0504	213	0.01
0.0755	306	−0.01
0.1	375	0.00
0.1255	433	0.01
0.1493	487	0.00
n-Heneicosane		
T = 320.05 K		
0.0167	93.2	−0.02
0.026	145	−0.05
0.0502	254	−0.02
0.0749	345	0.00
0.1002	423	0.01
0.1251	495	−0.01
T = 330.00 K		
0.0258	124	0.00
0.0507	227	0.01
0.0752	312	0.02
0.1003	388	0.01
0.125	462	−0.02
0.1397	498	−0.02
n-Docosane		
T = 320.05 K		
0.0249	144	−0.03
0.0521	274	−0.02
0.0736	365	−0.03
0.0998	440	0.00
0.1265	493	0.04
T = 330.00 K		
0.0261	131	0.01
0.0382	189	−0.01

(continued)

Table 1
(Continued)

x [a]	h^E (J mol^{-1})	δ [b]
0.0501	241	−0.01
0.065	290	0.02
0.0756	327	0.02
0.0999	404	0.01
0.1259	477	−0.01
0.1458	522	−0.02
n-Tricosane		
T = 330.00 K		
0.027	151	−0.05
0.0543	271	−0.02
0.0796	361	0.00
0.1041	433	0.01
0.1199	475	0.00
0.1508	537	0.00
n-Tetracosane		
T = 330.00 K		
0.0236	129	0.03
0.0369	201	−0.01
0.052	268	0.00
0.0723	347	0.01
0.0911	411	0.00
0.107	457	0.00
0.1413	532	0.00
n-Pentacosane		
T = 330.00 K		
0.0317	181	0.01
0.0459	250	0.01
0.0742	369	0.00
0.1066	476	−0.01
0.1124	490	−0.01
0.1392	543	0.00

[a] Is the liquid-phase mole fraction of the alkane.
[b] Is the relative deviation from the smoothed values.

measured h^E at different temperatures. The case of *n*-hexadecane at three different temperatures, is shown in Fig. 2. h^E effectively decreases with T, at constant composition.

3.3. Variation of h^E with number of carbon atoms, n

As expected, excess enthalpy (at constant T, x) increases with the number of carbon atoms in the paraffinic compound. In Fig. 3, we have drawn the curves $h^E = f(n)$ for all the paraffins studied here, at T = 330.00 K, and x = 0.050, 0.075 and 0.100.

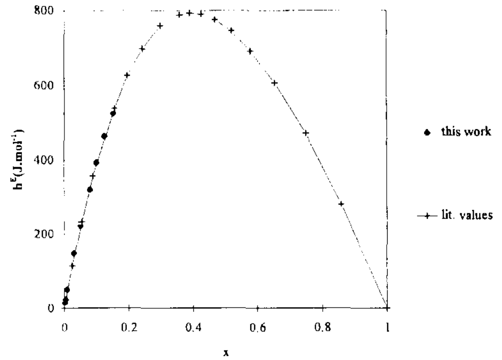

Fig. 1. Excess enthelpy of ethylbenzene + C_{16} at 298.15 K Comparison with literature values.

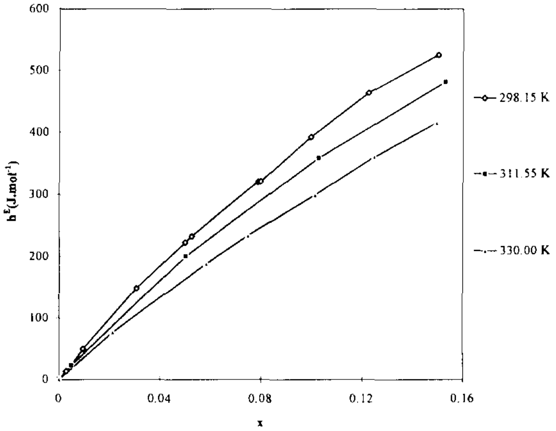

Fig. 2. $h^E(x)$ for *n*-hexadecane.

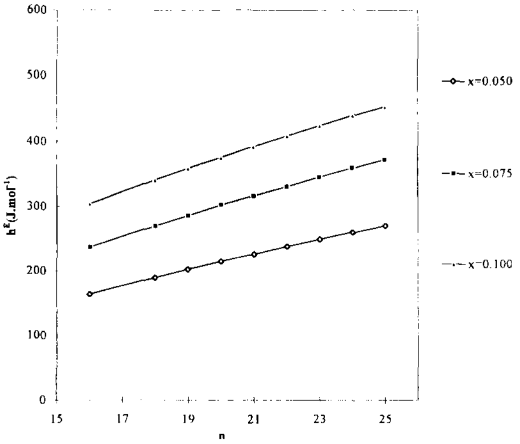

Fig. 3. $h^E(n)$ for different concentrations.

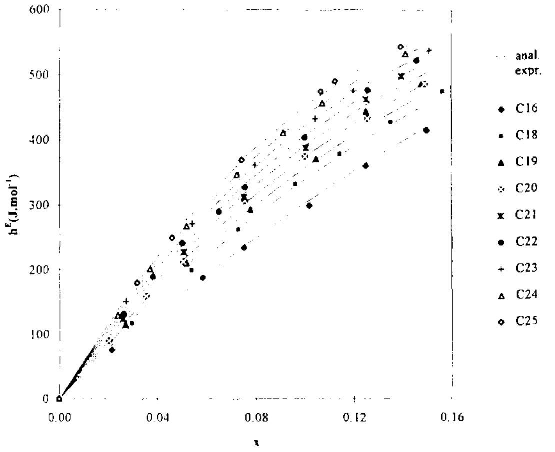

Fig. 4. $h^E(x)$ for all n-alkanes.

All the results of $h^E(x)$ at 330.00 K are shown in Fig. 4. In the composition interval studied, h^E indeed increases with n, at constant composition.

3.4. Analytical expression of $h^E(n,x,T)$

It was found necessary to fit our results with a simple expression, usable for all n-alkanes in the domains of temperature and composition studied. We chose a simple Margules-type expression of the form:

$$h^E(n,x,T) = x(1-x)[A(n,T) + (2x-1)B(n,T)]$$

where A and B, constants with respect to x, are functions of n and T, defined by:

$$A(n,T) = A_0 + A_1 n + A_2 T + A_3 T^2$$

$$B(n,T) = B_0 + B_1 n + B_2 n^2 + B_3 T$$

The numerical values of the constants $A_0 \ldots A_3$, $B_0 \ldots B_3$ are:

$A_0 = -40475\,\mathrm{J\,mol^{-1}}$
$A_1 = -329.8\,\mathrm{J\,mol^{-1}}\,(\text{carbon atom})^{-1}$
$A_2 = 268.9\,\mathrm{J\,mol^{-1}\,K^{-1}}$
$A_3 = -0.37\,\mathrm{J\,mol^{-1}\,K^{-2}}$
$B_0 = -16255\,\mathrm{J\,mol^{-1}}$
$B_1 = -791\,\mathrm{J\,mol^{-1}}\,(\text{carbon atom})^{-1}$
$B_2 = 3.6\,\mathrm{J\,mol^{-1}}\,(\text{carbon atom})^{-2}$
$B_3 = 82.6\,\mathrm{J\,mol^{-1}\,K^{-1}}$

The root mean square deviation was 0.024. The curves calculated by this expression for all n-alkanes studied at $T = 330$ K are shown in Fig. 4, with our experimental points.

3.5. Partial molar excess enthalpies at infinite dilution

For a better understanding of solution behaviour, it is advantageous to examine derivative excess properties in the limit of infinite dilution, where a single solute molecule is completely surrounded by solvent. In the dilute region where h^E is measured (our case here), the excess partial molar enthalpy of any paraffin i is given by:

$$h_i^E = h^E + (1-x)\left(\frac{\partial h^E}{\partial x}\right)_{n,T} = (1-x)^2[A(n,T) + (4x-1)B(n,T)]$$

The partial molar excess enthalpy at infinite dilution is given by:

$$h_i^{E\infty} = \lim_{x\to 0} h_i^E = A(n,T) - B(n,T)$$

such that:

$$h_i^{E\infty} = A_0 - B_0 + (A_1 - B_1)n + (A_2 - B_3)T - B_2 n^2 + A_3 T^2$$

Some values of $h_i^{E\infty}$ are plotted in Fig. 5 as a function of n, for $T = 298.15$, 310 and 330 K.

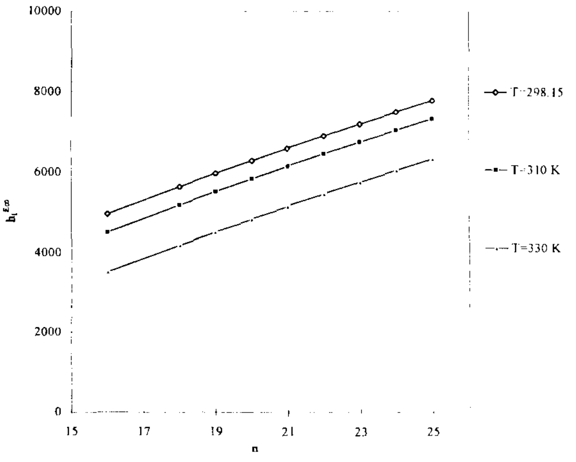

Fig. 5. Partial molar excess enthalpies at infinite dilution.

4. Conclusion

The h^E data reported here are the first of their kind in the study of *n*-alkanes having between 18 and 25 carbon atoms. They should have a tremendous potential for understanding the behaviour of *n*-alkane solutions at temperatures below and about the ambient. It is hoped that these experimentally-obtained data will help in the examination of predictive models currently being used to represent chemical potentials of multicomponent mixtures.

It will be interesting to measure the excess enthalpy in ternary solutions in which two of the components are *n*-alkanes. In this case, the behaviour of *n*-alkane binary liquid mixtures should be first studied. The influence of their mutual interaction may be important, or hopefully, negligible.

Simple analytical expressions are established to describe these excess properties in a second article [24].

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