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Dissolution of some normal alkanes in ethylbenzene: deduction of the enthalpy of mixing two *n*-alkanes in the solid state

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Abstract

Drop calorimetry has been used to measure the heat changes occurring upon the dissolution of some single *n*-alkanes (octadecane to tetracosane) or their binary mixtures ($C_{22}H_{46}$–$C_{24}H_{50}$ and $C_{23}H_{48}$–$C_{24}H_{50}$), in ethylbenzene, at 311.45 K. The enthalpy changes measured show the even-odd alternation effect known for *n*-alkanes. The binary mixtures show pronounced non-ideality. Their enthalpies of formation at 293.15 K were deduced from the measurement of their heats of dissolution in ethylbenzene and found to depend on the crystal type. It is shown that these mixtures may consist of several phases of solid solutions. © 1997 Elsevier Science B.V.

Keywords: Binary mixtures; Drop calorimetry; Enthalpy of formation; Even-odd alternation effect; Excess functions; Experimental; *n*-alkanes

1. Introduction

Normal paraffins have been the subject of structural and physico–chemical investigations over the last decades. These organic compounds are involved in a number of syntheses, and are known to be at the origin of problems encountered in the petroleum industry during the extraction and refining of oil, as well as the vaporization of finished products. In effect, *n*-paraffins having carbon atoms between 18 and 24 in their aliphatic chains, form wax crystals in fuel at low temperatures. The solutions sought by refiners consist of the reduction of fuel crystallizing temperatures through the use of cloud and pour-point depressant additives.

In this laboratory, we have a plan for a complete thermodynamic study in which the structures of the pure *n*-alkanes and their mixtures could be related to their thermochemical properties. These structure–property relationships could finally lead to a better understanding of fuel properties and behaviour. For this purpose, it is necessary to study simple systems by experiment.

This paper deals with experimental investigations of the heat changes involved when a solid *n*-alkane or mixture of *n*-alkanes, initially at a temperature of 293.15 K, is dropped into a solvent maintained in a Calvet-type microcalorimeter at 311.45 K. These heat

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changes permit the calculation of the enthalpies of formation of a binary mixture at the initial temperature.

As solvent, we have chosen ethylbenzene, an organic compound having an aromatic nucleus and an aliphatic side-chain. We have hitherto studied the pure *n*-alkanes from octadecane ($C_{18}H_{38}$) to tetracosane ($C_{24}H_{50}$) and two of their binary mixtures (C_{22}–C_{24} and C_{23}–C_{24}). Our data indicate the possibility of multisolid-phases of binary paraffinic mixtures in the aromatic solvent.

2. Experimental

The method used consists in dropping a solid sample (initially at temperature T_i =293.15 K) into a bath of solvent maintained at T_f =311.45 K in the calorimeter. The thermal effects produced are related to the enthalpies of mixing: the variation of the molar enthalpy of the product between the solid state at T_i and the dissolved state at T_f, is calculated from the quantity of heat absorbed by the dissolution of the sample, divided by the number of moles of the latter.

2.1. Apparatus

The experimental device is composed principally of a Calvet-type microcalorimeter of very high sensitivity, a SETARAM RT 3000 RA temperature-regulator, an amplifier-integrator and a SEFRAM recorder. The set-up is outlined in detail by Belaadi [1] and by one of the authors, Ghogomu [2].

2.2. Chemicals

All the *n*-alkanes received from Aldrich (Steinheim, Germany) were used without further purification. The purity grades, checked by gas chromatography, were 99 per cent minimum. Ethylbenzene from Aldrich (Steinheim, Germany) had a purity grade of 99.8 per cent. Gallium used as standard, was provided by Alusuisse with a purity of 99.9999 per cent, while copper was a grade 1 puratronic speciality product obtained from Johnson Matthey (UK) to serve as sample container.

2.3. Operating conditions and standardization

The solution in the measuring cell was constantly stirred during the experiments. This helped to homogenize the solution. The total amounts of *n*-paraffins used were such that the final solutions were dilute (mole fractions less than 0.002). In order to avoid the flotation of the samples, the *n*-paraffins or mixtures were placed on thin plates of copper foil. For this, the products were melted in a spatula, then filled into the plate and left to solidify.

The quantity of heat involved Q, is directly proportional to the number of integrator units I:

$$Q = q \cdot I$$

where q is the proportionality constant obtained by standardization of the calorimeter. This was done by using a very pure sample of gallium under the same operating conditions as those given above. The thermodynamic properties of gallium were read from the tables of Hultgren et al. [3]. The value of q obtained was

$$q = (3.246 \pm 0.003) 10^{-2} \text{ Joule per integrator unit}$$

2.4. Calculation of heat changes

The total thermal effect measured is the sum of two distinct processes; first the heating-up of the copper plate from T_i to T_f, then the change of state of the *n*-paraffins from solid at T_i to the dissolved state at T_f in four steps:

1. heating-up of the solid from T_i to the melting point, T_m,
2. melting at T_m,
3. heating (or cooling) of the liquid from T_m to T_f,
4. dilution in ethylbenzene.

The contribution of the copper plate was determined beforehand and found to be

$$I_{Cu} = (0.208 \pm 0.001) * m_{Cu}$$

where I_{Cu} is the number of integrator units, and m_{Cu} is the mass of the plate in mg. If I_{tot} is the total number of integrator units obtained, then the contribution of the paraffinic product I_p, is

$$I_p = I_{tot} - I_{Cu}$$

Finally, the variation of the molar enthalpy of the paraffin is given by the expression:

$$\Delta H_p = \frac{q \cdot I_p}{N_p} \text{ J.mol}^{-1}$$

where N_p is the number of moles of the paraffinic sample.

3. Experimental results and observations

Except for octadecane, all the normal alkanes studied here exhibit a solid-phase transition a few degrees below their melting points. The transition and melting points reported in the literature [4,5,12–14], are shown on Table 1.

The thermal effect can be defined by the enthalpy difference :

$$\Delta H_p = H(\text{solution}, T_f) - [H(\text{solid solute}, T_i) + H(\text{liquid solvent}, T_f)]$$

For each solute–solvent couple, we carried out five or six measurements. For very dilute solutions (x<0.002), the molar heat changes observed do not depend on the concentration of the paraffin solute as pointed out by Belaadi [1]. The algebraic averages of the experimental results are given in Tables 1–3. The absolute error on each value is less than 0.05 KJ.mol^{-1}.

Table 1
Experimental results of the heat changes (ΔH_p) measured when an n-alkane initially in the solid state at 293.15 K is dissolved in ethylbenzene at 311.45 K. T_t and T_m are the transition and melting point temperatures in K

n	ΔH_p/J.mol^{-1}	T_t/K	T_m/K	h_i^{∞}/J.mol^{-1}
18	76.130	—	301.15	5130.67
19	77.636	295.15	305.15	5458.69
20	84.837	309.35	309.55	5779.50
21	86.504	305.65	313.55	6093.08
22	94.075	316.50	317.55	6399.44
23	94.990	313.45	320.55	6698.58
24	103.171	320.85	324.25	6990.51

Table 2
Experimental results of the heat changes (ΔH_p) measured when a solid binary mixture of docosane and tetracosane (initially at T=293.15 K) is dissolved in ethylbenzene at 311.45 K. Y is the mole fraction of tetracosane in the original binary mixture.

Y	ΔH_p/J.mol^{-1}
0.0000	94.075
0.0272	90.215
0.0504	88.315
0.0699	88.363
0.0801	86.765
0.0900	88.391
0.0999	87.721
0.1151	86.980
0.1303	86.461
0.1500	87.689
0.1747	87.317
0.2030	87.109
0.3003	86.245
0.3497	87.000
0.3998	88.180
0.5290	90.211
0.5755	90.377
0.5999	91.306
0.6750	92.488
0.7350	93.871
0.7999	95.202
0.9000	99.093
1.0000	103.171

Table 3
Experimental results of the heat changes (ΔH_p) measured when a solid binary mixture of tricosane and tetracosane (initially at T=293.15 K) is dissolved in ethylbenzene at 311.45 K. Y is the mole fraction of tetracosane in the original binary mixture

Y	ΔH_p/J.mol^{-1}
0.0000	94.990
0.0497	92.990
0.1002	92.726
0.2000	92.867
0.3500	93.906
0.5001	93.725
0.6001	94.593
0.7001	95.651
0.7500	98.065
0.7998	99.160
0.9000	101.507
0.9500	101.573
1.0000	103.171

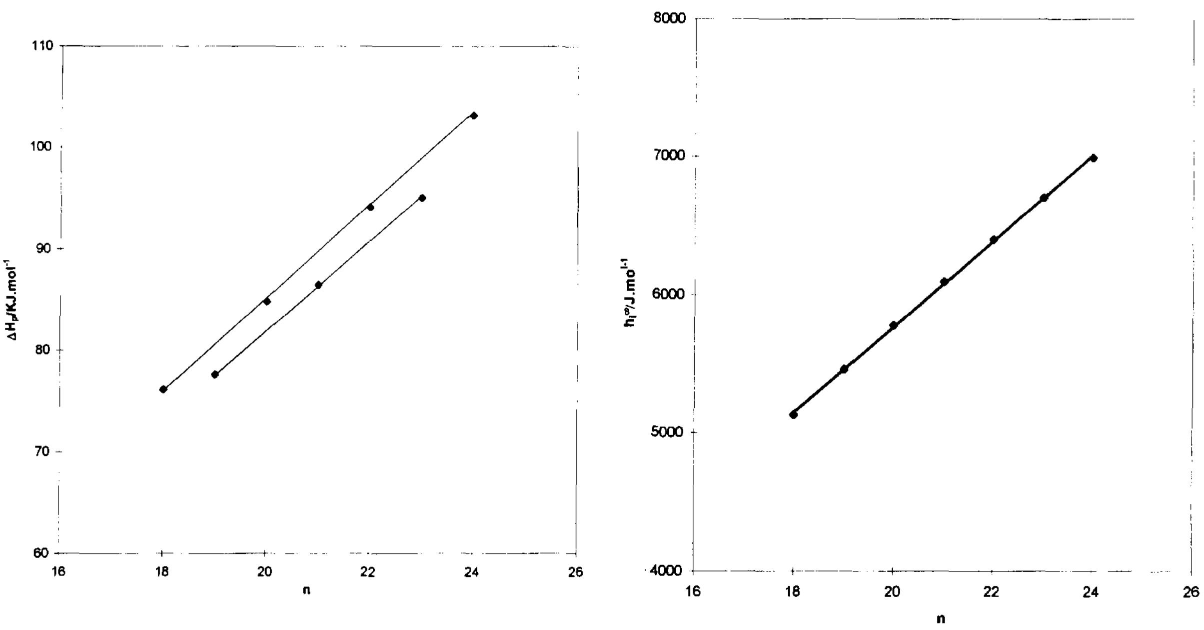

Fig. 1. (a) Experimental results of the heat changes (ΔH_p/KJ.mol^{-1}) involved when pure n-alkanes go from the solid state at 293.15 K to the liquid state dissolved in ethylbenzene at 311.45 K. n is the number of carbon atoms in the aliphatic chain of paraffins. (b) Variation of the excess enthalpy at infinite dilution h_i^∞ with the number of carbon atoms n.

3.1. Pure n-alkanes

We have plotted the values of ΔH_p against the number of carbon atoms in the molecule, n (Fig. 1 a). Two straight lines may be drawn: one for the even-numbered n-alkanes and another for the odd-numbered homologues. There is clearly an even-odd alternation effect, analogous to that of the other properties of the homologous series of n-alkanes. The difference in heat changes measured here (between even-and odd-numbered compounds), is about 3 to 3.5 KJ.mol^{-1} at equivalent values of n.

3.2. Binary mixtures of n-alkanes

The solid binary mixture samples were prepared by melting appropriate proportions of the pure components. After thoroughly mixing, the homogeneous liquid solution was quenched in a crystallizing dish maintained at a very low temperature in a Dewar vessel containing liquid air. Such a rapid cooling ensured uniform steric concentration of each component in the solid state.

Two binary mixtures were studied: first, two even-numbered n-alkanes (C_{22}–C_{24}), then an odd-numbered n-alkane with its even-numbered consecutive homologue (C_{23}–C_{24}). Our results are presented as curves of ΔH_pversus Y, the mole fraction of tetracosane in the binary mixture (Figs. 2 and 3).

These curves show that the variations of the thermal effects with composition are not linear. It follows that the binary solid mixtures of the paraffins are not ideal. This could also mean that at certain compositions there would be coexistence of two distinct solid phases, as reported from crystallographic studies by Hasnaoui [6], Denicolo et al. [7] and by Dirand et al. [8–10].

4. Excess enthalpy at infinite dilution, h_i^∞

The heat change occurs upon mixing a very small quantity of liquid solute (i) in the solvent. It is the

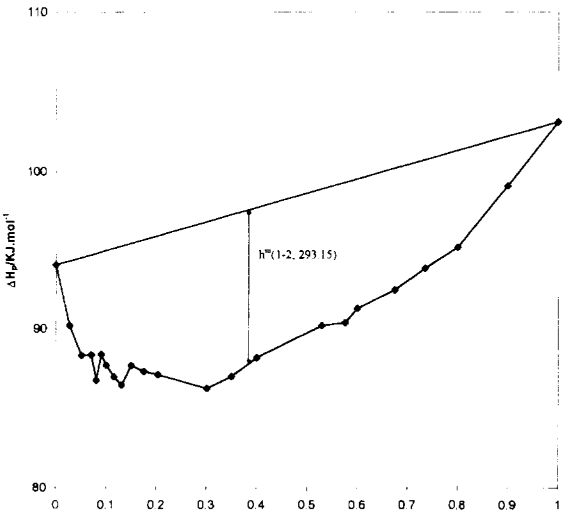

Fig. 2. Heat changes (ΔH_p/KJ.mol^{-1}) observed when a solid binary mixture of docosane with tetracosane initially at temperature 293.15 K is dissolved in ethylbenzene at 311.45 K. The straight line represents ideal mixtures. The heat of formation of any solid binary mixture at 293.15 K may be calculated from the difference between this line and the curve, as shown.

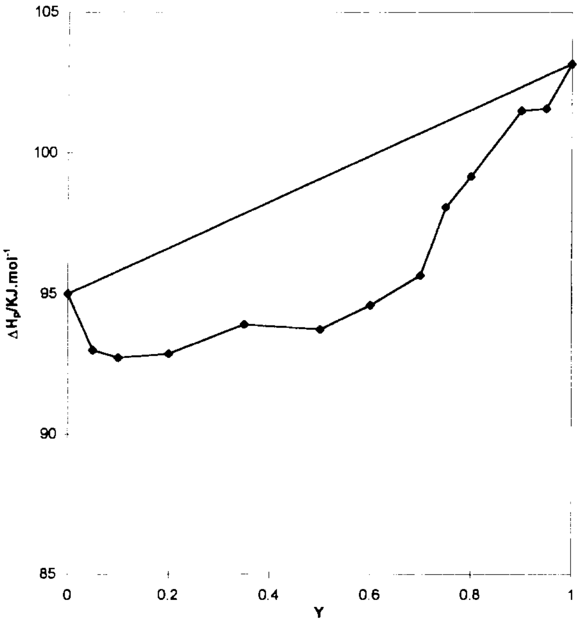

Fig. 3. Heat changes (ΔH_p/KJ.mol^{-1}) observed in the case of tricosane–tetracosane mixtures. The straight line represents values of hypothetical ideal mixtures.

partial molar excess enthalpy at infinite dilution. This heat change was determined from measurements of the enthalpy of mixing *n*-alkanes in ethylbenzene, using a SETARAM C80D Calorimeter [11].

The values of h_i^∞ for *n*-alkanes from C_{18} to C_{24} at 311.45 K are given in Table 1 and shown graphically in Fig. 1 b. There is a regular increase of this quantity with the number of carbon atoms *n*. It is important to note that h_i^∞ does not show any even-odd alternation.

5. Calculation of the heat of mixing

This quantity, which is also the heat of formation of a binary mixture from the two components at the same temperature, was calculated from the heat changes occurring upon the dissolution of pure alkanes and their binary mixtures, in ethylbenzene. In the following, 1 and 2 represent the two *n*-alkanes while 3 represents the solvent, ethylbenzene. The number of moles of each component i, is noted n_i (i = 1, 2, or 3).

5.1. Theory

For heat changes due to the mixture of an *n*-alkane in ethylbenzene (for example 1 in 3), the quantity ΔH_p may be expressed as

$$\begin{aligned}\Delta H_p(1\text{–}3) &= (n_3+n_1)H\,(\text{solution }1\text{–}3, T_f)\\ &\quad - n_3H(\text{liq. }3, T_f) - n_1H(\text{sol. }1, T_i)\end{aligned} \tag{1}$$

Reducing this expression to one mole of paraffin 1, we have

$$\begin{aligned}h(1\text{–}3) &= \frac{\Delta H_p\,(1\text{–}3)}{n_1}\\ &= \frac{n_3+n_1}{n_1}H\,(\text{solution }1\text{–}3, T_f)\\ &\quad -\frac{n_3}{n_1}H\,(\text{liq. }3, T_f) - H\,(\text{sol. }1, T_i)\end{aligned} \tag{2}$$

Using the heat of mixing at T_f defined by

$$\begin{aligned}\Delta H^m(1\text{–}3, T_f) &= (n_3+n_1)H\,(\text{solution }1\text{–}3, T_f)\\ &\quad - n_3H\,(\text{liq. }3, T_f)\\ &\quad - n_1H\,(\text{liq .}1, T_f)\end{aligned} \tag{3}$$

The expression of $h(1\text{–}3)$ becomes

$$h(1\text{–}3) = \frac{\Delta H^m(1\text{–}3, T_f)}{n_1} + [H(\text{liq}.3, T_f) - H(\text{sol}.1, T_i)] \qquad (4)$$

At infinite dilution ($n_1 \ll n_3$), we may write

$$\frac{\Delta H^m(1\text{–}3, T_f)}{n_1} \approx \frac{\partial \Delta H^m(1\text{–}3, T_f)}{\partial n_1} = h_1^m(1\text{–}3, T_f) \qquad (5)$$

where $h_1^m(1\text{–}3, T_f)$ represents the partial molar enthalpy due to mixing 1 in 3 at the temperature T_f. If n_1 approaches 0, then $h_1^m(1\text{–}3, T_f) \to h_1^\infty$ and the expression of $h(1\text{–}3)$ becomes

$$h(1\text{–}3) = h_1^m(1\text{–}3, T_f) + H(\text{liq}.1, T_f) - H(\text{sol}.1, T_i) \qquad (6)$$

For the dissolution of paraffin 2 in solvent 3, we will have

$$h(2\text{–}3) = h_2^m(2\text{–}3, T_f) + H(\text{liq}.2, T_f) - H(\text{sol}.2, T_i) \qquad (7)$$

In the case of the dissolution of a binary mixture of paraffins (1+2) in ethylbenzene, the heat effects measured can be expressed as

$$\Delta H_p(1\text{–}2\text{–}3) = (n_1 + n_2 + n_3)H(\text{solution } 1\text{–}2\text{–}3, T_f) - n_3 H(\text{liq}.3, T_f) - (n_1 + n_2)H(\text{sol}.\ 1\text{–}2, T_i) \qquad (8)$$

Reducing to one mole of mixture, this expression becomes

$$h(1\text{–}2\text{–}3) = \frac{\Delta H_p(1\text{–}2\text{–}3)}{n_1 + n_2} = \frac{n_1 + n_2 + n_3}{n_1 + n_2} H(\text{solution } 1\text{–}2\text{–}3, T_f) - \frac{n_3}{n_1 + n_2} H(\text{liq}.3, T_f) - H(\text{sol}.\ 1\text{–}2, T_i) \qquad (9)$$

Using partial molar quantities in the ternary mixture, we may write

$$h(1\text{–}2\text{–}3) = \frac{1}{n_1 + n_2}[n_1 h_1^m(1\text{–}2\text{–}3, T_f) + n_2 h_2^m(1\text{–}2\text{–}3, T_f) + n_3 h_3^m(1\text{–}2\text{–}3, T_f)] + \frac{n_1}{n_1 + n_2}[H(\text{liq}.1, T_f) - H(\text{sol}.\ 1, T_i)] + \frac{n_2}{n_1 + n_2}[H(\text{liq}.\ 2, T_f) - H(\text{sol}.\ 2, T_i)] - h^m(\text{sol}.\ 1\text{–}2, T_i) \qquad (10)$$

where $h^m(\text{sol. } 1\text{–}2, T_i)$ is the heat of mixing solids 1 and 2 at temperature T_i. This quantity has as expression

$$h^m(\text{sol}.1\text{–}2, T_i) = \frac{1}{n_1 + n_2}[(n_1 + n_2)H(\text{sol}.\ 1\text{–}2, T_i) - n_1 H(\text{sol}.\ 1, T_i) - n_2 H(\text{sol}.\ 2, T_i)] \qquad (11)$$

It represents the enthalpy of formation of the solid mixture at T_i =293.15 K.

Next we choose a Redlich–Kister expression to describe the liquid-state mixing quantity

$$h_m(1\text{–}2\text{–}3, T_f) = x_1 x_3 H_1 + x_2 x_3 H_2 + x_1 x_2 H_{12} + \phi(x_1, x_2, x_3) \qquad (12)$$

where $H_1 = h_1^m(1\text{–}3, T_f)$, $H_2 = h_2^m(2\text{–}3, T_f)$ and $H_{12} = h^m(1\text{–}2, T_f)$

For very dilute solutions (when x_1 and x_2 tend to zero), the partial molar quantities become:

$$h_1^m(1\text{–}2\text{–}3, T_f) = H_1$$

$$h_2^m(1\text{–}2\text{–}3, T_f) = H_2$$

$$h_3^m(1\text{–}2\text{–}3, T_f) = 0$$

Also,the ternary interaction term $\phi(x_1, x_2, x_3)$ is negligible in this case.

Using y_1 and y_2 as mole fractions of paraffins 1 and 2 in the solid binary mixture

$(y_1 = n_1/(n_1 + n_2)$ and $y_2 = n_2/(n_1 + n_2))$

$$\begin{aligned} h(1\text{–}2\text{–}3) = {} & y_1H_1 + y_2H_2 + y_1(H(\text{liq}.1, T_f) \\ & - H(\text{sol}.\,1, T_i)) + y_2(H(\text{liq}.\,2, T_f) \\ & - H(\text{sol}.\,2, Ti)) \\ & - h_m(\text{sol}.\,1\text{–}2, T_i) \end{aligned} \tag{13}$$

This expression can also be written in terms of $h(1\text{–}3)$ and $h(2\text{–}3)$ defined by Eqn.(6) and Eqn. (7):

$$\begin{aligned} h(1\text{–}2\text{–}3) = {} & y_1h(1\text{–}3) + y_2h(2\text{–}3) \\ & - h^m(\text{sol}.\,1\text{–}2, T_i) \end{aligned} \tag{14}$$

The enthalpy of formation of the binary solid may thus be calculated from the expression

$$\begin{aligned} \Delta_fH^0(1\text{–}2, T_i) & = h^m(\text{sol}.\,1\text{–}2, T_i) \\ & = y_1h(1\text{–}3) + y_2h(2\text{–}3) \\ & \quad - h(1\text{–}2\text{–}3) \end{aligned} \tag{15}$$

This calculation is represented schematically on Fig. 2, as the difference between the ideal line joining the ΔH_p values of the pure components and the values for the binary mixtures at each composition.

6. Results

The heats of formation thus calculated are shown on Figs. 4 and 5 respectively for the C_{22}–C_{24} and C_{23}–C_{24} binary mixtures. In these figures $\Delta_fH^0(1\text{–}2,\ T_i)$ is plotted against y_2, the mole fraction of tetracosane in the binary solid.

These results show that the formation of binary mixtures from pure solid *n*-alkanes leads to an absorption of heat, the amount of which depends on the relative quantity of each component present. The heat absorbed may attain 10 KJ per mole of mixture. No simple and direct relation can be inferred between the heats of formation and the composition of the binary mixtures.

The shapes of the $\Delta_fH^0(1\text{–}2,\ T_i)$ versus y_2 plots however show irregular variations at certain composition intervals. We may deduce from this observation that the structures of the mixtures are not the same over the entire composition range. Some of the mixtures seem to show partial solubility of one paraffin in another, as in some liquid mixtures.

In effect, crystallographic and calorimetric studies carried out by Hasnaoui [6] on the C_{22}–C_{24} binary system show that nine regions are present on the phase diagram, four of them being two-phased. On the C_{23}–C_{24} binary system Denicolo et al. [7] mentioned the existence of a two-phase region on the phase diagram. More recently, several studies by

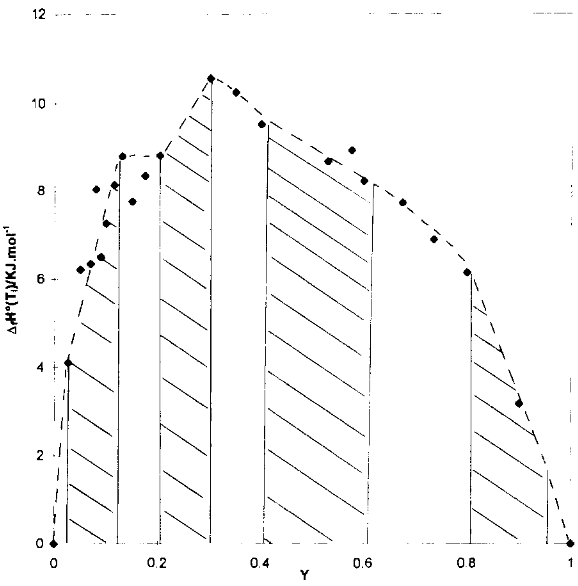

Fig. 4. Heats of formation of mixtures of docosane with tetracosane. The reported two-phase regions are shaded.

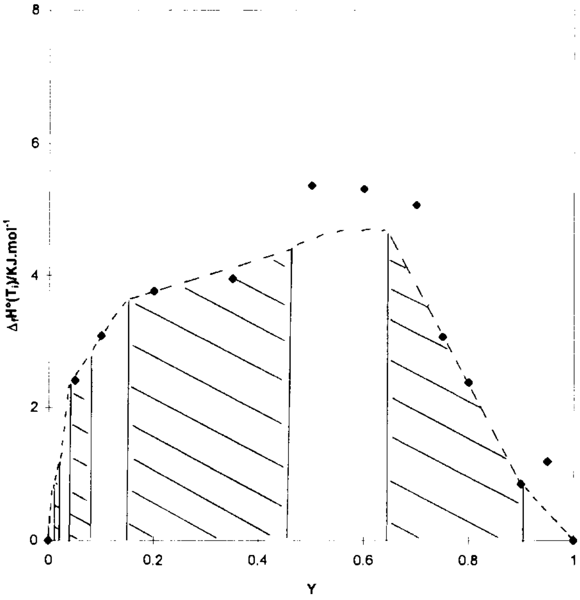

Fig. 5. Heats of formation of binary mixtures of tricosane with tetracosane. Two-solid-phase regions are shaded.

Dirand et al. [8–10] at "low temperatures" have shown that the phase diagrams are not so simple. On Fig. 4 and Fig. 5, we have shaded the two-phase regions corresponding to their diagrams at 293.15 K.

7. Discussion and Conclusion

The enthalpy measurements show the even-odd alternation effect of the homologous series of pure *n*-alkanes. The basis of this effect is the alternation of the molecular structure of the low-temperature stable solids (triclinic for paraffins with an even number of carbon atoms, and orthorhombic for those with an odd number).

The dissolution of binary mixtures of *n*-alkanes in ethylbenzene shows that these mixtures are not ideal. The heats of mixing (in this case equal to the heats of formation) calculated from our results show that one-phase and two-phase regions could be present on the binary phase diagrams at 293.15 K. In effect, the heat of formation would vary linearly with composition if the mixture consists of two distinct solid phases. This paper proves that this is not so, and indeed the mixture may consist of several phases of solid solutions.

It is interesting to point out that Won [15,16] postulated that the paraffinic wax phase consists of a single homogeneous solid solution. Hansen et al. [17], Pedersen et al. [18,19] and Pedersen [20] used essentially the same concept of a single solid solution phase in order to calculate the cloud point and wax formation from North Sea crude oils. Recently, Lira-Galeana et al. [21] proposed a multisolid-phase model to calculate the wax formation data reported by Hansen and Pedersen. However, there appears to be no predictive method to calculate the mutisolid-phases as functions of composition and temperature. In a future work, we will be measuring the coexisting solid phase compositions of binary, ternary or multicomponent mixtures.

8. Glossary

Definition of symbols

$h(1\text{–}3)$	Molar heat change upon mixing paraffin $(1, T_i)$ in ethylbenzene $(3, T_f)$
$h_1^m(1\text{–}3, T_f)$	Partial molar excess enthalpy of (1) in (3) at T_f
h_i^{∞}	Partial molar excess enthalpy at infinite dilution (of i in ethylbenzene)
$H(\text{sol.}1, T_i)$	Heat content of solid 1 at temperature T_i
$H(\text{solution } 1\text{–}3, T_f)$	Heat content of solution of (1) and (3) at temperature T_f
$\Delta_f H^0(1\text{–}2, T_i)$	Standard enthalpy of formation of binary mixture (1–2) at temperature T_i
ΔH^m	Total enthalpy of mixing (1) in (3)
$\Delta H_p(1\text{–}3)$	Heat change due to the dissolution of paraffin (1) at T_i in ethylbenzene(3) at T_i
I	Number of integrator units
m_{Cu}	Mass of copper plate
n	Number of carbon atoms in the molecule
q	Proportionality constant
Q	Quantity of heat involved in the process
T_f	Final temperature (maintained in the calorimeter)
T_i	Initial temperature of pure solid or solid binary mixture
T_m	Melting point
T_t	Solid-state transition temperature

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