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Variations of Dissolution Enthalpies of Pure *n*-Alkanes in Heptane as a Function of Carbon Chain Length

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Measurements of dissolution enthalpies in heptane at ambient temperature were carried out by mixing calorimetry on the *n*-alkanes going from $C_{20}H_{42}$ to $C_{36}H_{74}$. These dissolution enthalpy values increase linearly as a function of the carbon atom number. Furthermore, they reveal an alternating effect between odd- and even-numbered *n*-alkanes and highlight that the mixing of an *n*-alkane in the liquid phase with heptane is an athermal process: the variation of its enthalpy from the dissolution temperature up to its melting temperature corresponds to its dissolution enthalpy in heptane.

Introduction

n-Alkanes, in a natural state in the fluids of paraffinic crude and middle distillate fuels, are a recurring problem for refiners and diesel-fuel consumers because these saturated hydrocarbons have the property to crystallize when the temperature decreases, and form paraffinic solid deposits. The accumulation of these solid deposits, which clog up filters and obstruct pipelines during production or transport, leads inevitably to exploitation overcharges and could generate damage of industrial equipment. To be able to estimate the appearance temperature of these deposits, as well as their quantity, it thus becomes crucial to weigh the risks and, consequently, adapt the parameters of exploitation. This requires the development of a thermodynamic model which could predict the conditions of paraffinic deposit crystallization for a given fluid composition and for a given temperature. Determining the solid deposit curve requires knowing all of the thermodynamic properties (phase change data, solubility, heat capacities) of the pure compounds occurring in the solid/liquid equilibrium.

From this point of view, the measurements of the solubility of *n*-alkanes in various solvents, obtained by varying either the carbon chain length of the *n*-alkane or the nature of the solvent used (polar, apolar solvents or mixtures of solvents), are very numerous[1−21] because they constitute an essential data bank for the development of thermodynamic models able to represent the solubility equations or the solid/liquid equilibrium.

Thus, to increase the size of this data bank and to have a reliable set of solubility results for testing the predictive capacities of thermodynamic models, we have measured the dissolution enthalpies in heptane (C_7H_{16}) of several saturated aliphatic hydrocarbons: *n*-alkanes with chain lengths ranging from 20 to 36 carbon atoms. This study will also permit the establishment of a relation between the dissolution enthalpy and the carbon atom number, a relation useful to simplify the future thermodynamic model use.

Principle of Measurement and Operating Conditions

All chemicals were purchased from Fluka and were used as delivered without further purification. Their purities were at least better than 98%. *n*-Alkanes, whose formula is C_nH_{2n+2}, are hereafter denoted by C_n for simplification, *n* being the carbon atom number of the chain.

Enthalpies of dissolution were measured using a Setaram C80 differential calorimeter. The solid sample and the solvent are initially in two perfectly separated compartments of the cell, and the mixture is made by reversal of the calorimeter. The scheme of the cell is given in Figure 1. The separation between the lower and the upper compartments of the cell is realized by a mercury joint (Figure 1). A differential assembly involves the presence of two cells in the calorimeter: the measurement cell, containing the sample to be analyzed and the solvent, and the reference cell, filled only with solvent. To accurately measure the enthalpy of dissolution of the sample and to minimize the asymmetry effect of the two cells (the cells are linked in opposition), the quantities of material (sample, solvent, and mercury) must be identical between each compartment of the two cells, the solid reagent mass in the measurement cell being replaced by an equivalent mass of solvent in the reference cell.

The reversal of the calorimeter is released after acquisition of a linear stable baseline. The dissolution of the pure C_n's in C_7 is associated, in each case, with an endothermic effect. The measurement of the enthalpy of dissolution is obtained by the integration of the calorimetric signal, by extrapolating a linear baseline from two points chosen judiciously on both sides of the endothermic peak of dissolution.

The experimental conditions are the following: all experiments are performed at the temperature 296.15 K; the solvent is heptane C_7H_{16} (purity $\geq$ 99%); the reagent quantities are 9.3 mg for the solid C_n and 3 g for the solvent C_7; before dissolution, all C_n's are in the solid state and in an ordered phase of low temperatures; all experimental values of the enthalpies of dissolution are the average of two very close measurements, deduced from two reproducible experiments; the experiments are carried out under atmospheric pressure (the increase of pressure has an effect

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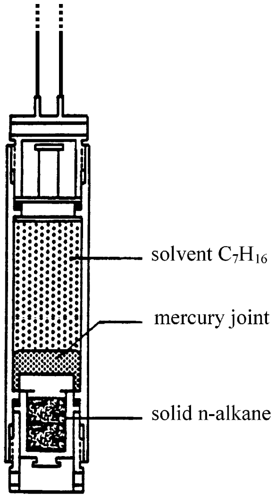

Figure 1. Calorimetric cell used in mixing calorimetry.

on the quantity and the nature of the solid paraffinic deposits similar to that induced by a decrease of temperature[22]).

The analysis temperature of 296.15 K is the lowest temperature, obtained without difficulty (throughout the whole experiment) and without modifying the experimental device, which allows us to analyze a wide range of pure C_n's in the solid state. Heptane is used here as solvent because it is cheap and nontoxic. Furthermore, a significant difference between the carbon atom numbers of the solvent and the studied C_n decreases the risk of forming a possible solid solution and improves the dissolution without increasing the temperature. The masses of reagent and solvent are chosen so as to have a total dissolution of the C_n in the solvent, whatever the C_n's molar mass, and in the entire chain length range studied here.

The comparison of our experimental dissolution enthalpies to those found in the literature[2,3,12] give a percentage difference of around 7%. This value seems high but in fact does not have real meaning: indeed, all the literature dissolution enthalpy data were obtained from solubility measurements, by extrapolating the slope of the straight line representing the logarithm of the solubility as a function of the temperature; so, to the uncertainties of the solubility measurements should be added the lack of precision of the slope determination. Our dissolution enthalpy results are directly calculated by the calorimeter by integration of the endothermic effect, so these data should be more accurate. It is difficult to give a meaningful percentage difference for our calorimetric analyses because the papers dealing with C_n dissolution enthalpy studies in C_7 by mixing calorimetry are very scarce. Thus, we can only point out that our dissolution enthalpy values are reproducible with a margin of error lower than 3% (deduced from two successive measurements). The precision of the experimental temperature was within ±0.2 K of the set point.

Results

The molar $\Delta_{\text{diss}}H$ and massic $\Delta_{\text{diss}}h$ experimental enthalpies of dissolution of all C_n's ranging from $C_{20}H_{42}$ to $C_{36}H_{74}$ are given in Table 1, with, for further information, the mole fraction in C_n (x_1) of each binary system C_n/C_7. Figure 2 represents the variations of the $\Delta_{\text{diss}}H$ experimental molar enthalpy of dissolution according to the n_c carbon atom number (at ambient temperature $T = 296.15$ K).

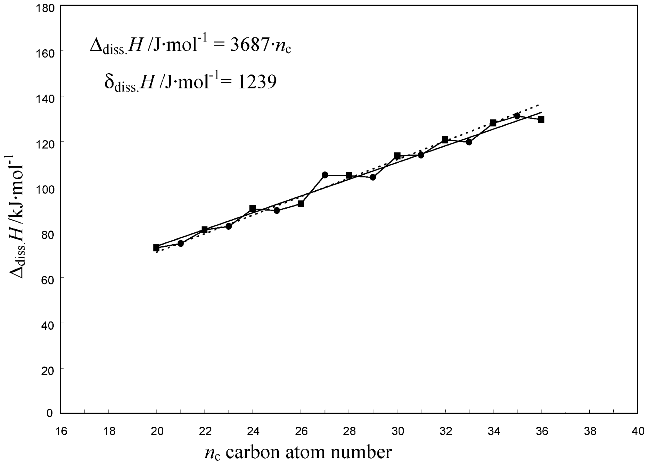

Figure 2. Variation of the experimental molar enthalpy of dissolution $\Delta_{\text{diss}}H$ according to the carbon atom number n_c (T = 296.15 K): —, linear fitting $\Delta_{\text{diss}}H$; ···, linear fitting Δ_o^1H.

Table 1. Molar and Massic Enthalpies of Dissolution of C_n's (1) in C_7 (2) (T = 296.15 K)

C_n	$100x_1$	$\Delta_{\text{diss}}h$/J·g^{-1}	$\Delta_{\text{diss}}H$/J·mol^{-1}
$C_{20}H_{42}$	0.106	259	73 126
$C_{21}H_{44}$	0.100	253	74 932
$C_{22}H_{46}$	0.095	261	80 918
$C_{23}H_{48}$	0.092	254	82 566
$C_{24}H_{50}$	0.087	267	90 321
$C_{25}H_{52}$	0.085	254	89 502
$C_{26}H_{54}$	0.080	252	92 463
$C_{27}H_{56}$	0.077	276	105 160
$C_{28}H_{58}$	0.076	266	104 920
$C_{29}H_{60}$	0.073	255	104 118
$C_{30}H_{62}$	0.071	268	113 505
$C_{31}H_{64}$	0.069	261	114 013
$C_{32}H_{66}$	0.066	268	120 771
$C_{33}H_{68}$	0.064	257	119 692
$C_{34}H_{70}$	0.063	267	128 057
$C_{35}H_{72}$	0.056	266	131 145
$C_{36}H_{74}$	0.051	256	129 623

Note: The carbon atom number range studied is limited to these 17 C_n's because C_n's with chain lengths lower than 20 carbon atoms are in the liquid state at the study temperature (296.15 K) and, for the C_n's with carbon atom number higher than 36, we encountered difficulties to obtain a complete dissolution of the sample with similar quantities of reagent.

Discussion

These results highlight a slight alternating effect between the enthalpies of dissolution of the even- and the odd-numbered C_n's. Indeed, we notice that the dissolution enthalpies of the even-numbered C_{2p}'s are located on a straight line which is above that of the odd-numbered C_{2p+1}'s, these two lines being parallel. This observation is close to that previously reported by Ghogomu,[14,23,24] who has already shown that odd-numbered C_{2p+1}'s are more soluble than even-numbered ones. The explanation of that alternating effect lies in the difference of the structures of the low temperature ordered phases according to the carbon atom number parity. Thus, even-numbered C_{2p}'s are in a triclinic structure γ_0 ($P\bar{1}$) for $20 \leq n_c$ (C_{2p}) ≤ 26 and in a monoclinic structure δ_0 ($P2_1/a$) for $28 \leq n_c$ (C_{2p}) ≤ 36. In these two structures, the carbon chain axes are tilted with regard to the lamellar surface (tilted unit cell). All the odd-numbered C_{2p+1}'s are in an orthorhombic structure β_0 ($Pbcm$) for $21 \leq n_c$ (C_{2p+1}) ≤ 35, with the carbon chain axes perpendicular to the lamellar surface (rectangular unit cell).

In fact, these two types of structure, with tilted and rectangular unit cells, induce different densities, as we can

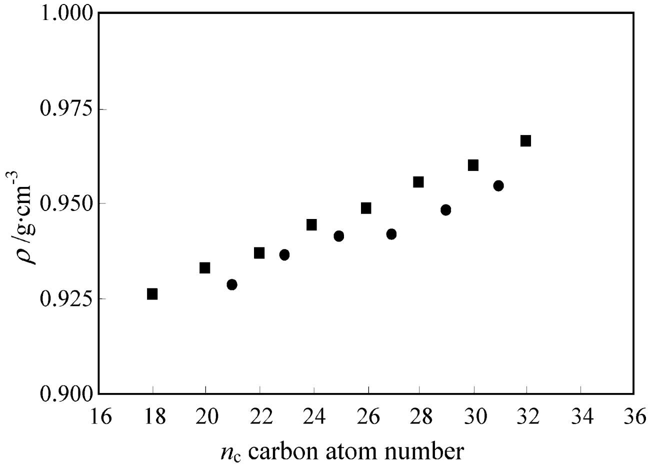

Figure 3. Alternation of the relative density ρ according to the carbon atom number parity: ●, $\rho(C_{2p+1})$; ■, $\rho(C_{2p})$.

see in Figure 3, which represents the variations of the relative density ρ as a function of the n_c carbon atom number and its parity (at ambient temperature). These data of relative density were calculated from the crystallographic parameters, obtained by Craig[25] for the triclinic, monoclinic, and orthorhombic structures as functions of the carbon atom number.

So, the crystals of the odd-numbered C_{2p+1}'s, with orthorhombic structures, are less dense and have, consequently, a lower cohesive energy than even-numbered C_{2p}'s. They are thus more soluble and have a lower enthalpy of dissolution.

For simplification, we opted for a single average representation for all odd- and even-numbered C_n's. So, the fitting of a linear equation on our experimental enthalpies, according to the n_c carbon atom number, gives the following result:

$$\text{For } 20 \le n_c \le 36: \quad \Delta_{diss}H/\text{J·mol}^{-1} = 3687 n_c \qquad (\delta_{diss}H/\text{J·mol}^{-1} = 1239)$$

For comparison, we have superposed, in Figure 2, the variations of the total enthalpy $\Delta_o^l H$ of the pure C_n's to the variations of the enthalpy of dissolution $\Delta_{diss}H$, as a function of n_c carbon atom number. The total enthalpy $\Delta_o^l H$ corresponds to the variation of enthalpy from the T_{o-d} order/disorder transition temperature up to the melting temperature T_{fus}. This enthalpy variation can be decomposed into the following thermodynamic terms:

$$\Delta_o^l H = \Delta H_{o-d} + \int_{T_{o-d}}^{T_{fus}} C_{p(R1)}\,\mathrm{dT} + \Delta_{fus}^d H + \left(\int_{T_{o-d}}^{T_{d-d}} C_{p(R1)}\,dT + \Delta H_{d-d} + \int_{T_{d-d}}^{T_{fus}} C_{p(R2)}\,\mathrm{dT}\right)$$

with ΔH_{o-d} and ΔH_{d-d} being the enthalpies of order/disorder and disorder/disorder solid/solid transitions, T_{o-d} and T_{d-d} being the temperatures of the order/disorder and disorder/disorder solid/solid transitions, $\Delta_{fus}^d H$ being the enthalpy of melting of a high temperature disordered rotator phase, T_{fus} being the melting temperature, $\int_{T_{o-d}}^{T_{fus}} C_{p(R1)}\,dT$, $\int_{T_{o-d}}^{T_{d-d}} C_{p(R1)}\,dT$, and $\int_{T_{d-d}}^{T_{fus}} C_{p(R2)}\,dT$ being the enthalpy consumption in the temperature domains of rotator phases, and $C_{p(R1)}$ and $C_{p(R2)}$ being the heat capacities of the disordered rotator phases, differing by their structure.

Note: The *n*-alkane C_{20} melts without undergoing any order/disorder transition; thus, the total enthalpy is equal to the melting enthalpy ($\Delta_o^l H = \Delta_{fus}^o H$ with $\Delta_{fus}^o H$ being the melting enthalpy of a low temperature ordered phase.

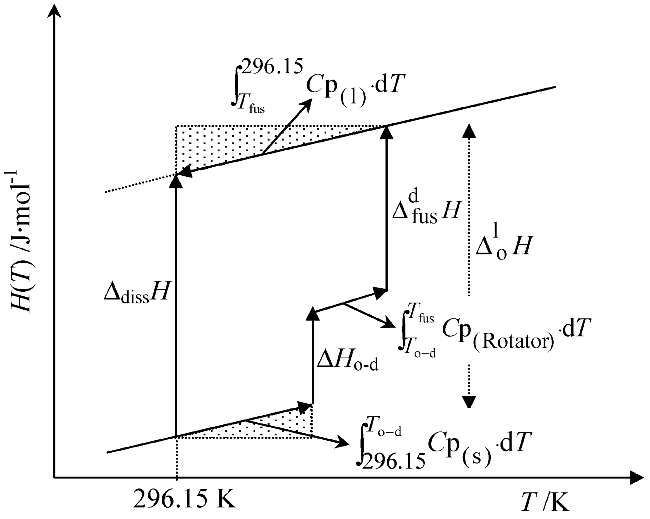

Figure 4. Decomposition of the enthalpy of dissolution $\Delta_{diss}H$ into its characteristic thermodynamic properties.

The study (experimental results, optimization, and comments) of these $\Delta_o^l H$ total enthalpy variations as a function of carbon atom number has already been developed in previous papers from our laboratory.[26-28]

In Figure 2, we notice that these two lines, representative of the molar dissolution $\Delta_{diss}H$ and the total $\Delta_o^l H$ enthalpy variations with respect to the carbon atom number, are very close and almost superposed. In fact, the enthalpy variation from the ordered phase of low temperatures up to the liquid phase, in the case of a given pure *n*-alkane, is equivalent to the enthalpy required to entirely dissolve this *n*-alkane in a solvent, at a reference temperature.

This observation induces the following comments: (i) The contribution of the difference ($\int_{T_{ref}}^{T_{o-d}} C_{p(s)}\,dT - \int_{T_{ref}}^{T_{fus}} C_{p(l)}\,dT$) ($C_{p(s)}$ and $C_{p(l)}$ being the C_n molar heat capacities respectively in the solid and the liquid state) to the dissolution enthalpy is negligible or within the margin of error for our measurements. To fix the ideas, the scheme of Figure 4 represents the different thermodynamic properties involved in the total and the dissolution enthalpy. (ii) The mixing of an *n*-alkane in the liquid phase with a solvent of the same nature (polarity, molecular shape) is an athermal process ($\Delta H_{liq}^{exc} = 0$, with ΔH_{liq}^{exc} the excess enthalpy in the liquid phase during the dissolution of the C_n's in C_7).

Conclusion

Measurements of the enthalpy of dissolution in C_7 of C_n's with carbon atom numbers going from 20 to 36 were carried out by mixing calorimetry at ambient temperature. These dissolution enthalpies increase linearly as a function of the molecular weight. Furthermore, these values highlight an alternating effect in regard to the carbon atom number parity, with the odd-numbered C_{2p+1}'s being more soluble than the even-numbered ones. Finally, since the values of the dissolution $\Delta_{diss}H$ and the total Δ_o^lH enthalpies as functions of carbon chain length are very close, we can conclude that the mixing of a liquid *n*-alkane with a hydrocarbon saturated solvent is an athermal reaction.

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