

CALORIMETRIC DETERMINATION OF THE HEATS OF DISSOLUTION OF STEARIC ACID IN SOME ORGANIC SOLVENTS

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ABSTRACT

The heats of dissolution of two stearic acid polymorphs were measured at 30.8°C in some organic solvents using a calorimetric technique.

For the C polymorph at a concentration of 0.02 mole l⁻¹, the heats of dissolution found are 64.6, 71.7, 75.1 and 74.0 kJ mole⁻¹ for decane, cyclohexane, methanol and butanone as solvent, respectively.

Using the same calorimeter, we obtained the heat of fusion for stearic acid as 62.6 ± 0.2 kJ mole⁻¹.

In decane and cyclohexane the heats of dissolution are increased over the heat of fusion by a partial dissociation of the stearic acid dimers. In methanol and butanone, a complete dissociation is followed by the formation of (weaker) hydrogen bonds between the solute and solvent.

The heat of polymorphic transformation from the B into C polymorph could be deduced from the difference in the heats of dissolution of the two polymorphs as 6.0 ± 0.6 kJ mole⁻¹.

INTRODUCTION

Stearic acid, CH₃(CH₂)₁₆COOH, occurs in three main polymorphic modifications, A, B and C. The latter two are easily crystallized and of interest to us.

The solubility of stearic acid in various organic solvents indicates variations from the ideal solubility [1]. Stearic acid forms cyclic dimers in the solid state [2]. The dimers may dissociate in solution and form complexes with the solvent, depending on the polarity of the solvent.

Little, if anything, is known of the physical chemistry of stearic acid

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solutions and specifically of the solute–solvent interactions.

We were interested in a direct measurement of the heats of dissolution (1) for a better understanding of the non-idealities in the solubilities and (2) because the heats of the solid–solution transition play a key role for the kinetics of crystal growth.

EXPERIMENTAL

The pure crystalline polymorphs B and C of stearic acid were prepared by recrystallization from benzene and pentane solution. The stearic acid used had a purity of > 99.6% (Fluka). The benzene and pentane had purities of > 99.7 and > 99%, respectively (both Fluka).

To obtain the pure B polymorph, stearic acid was crystallized at low supersaturation from benzene at 20°C. The solution was kept for 2 to 3 days at this temperature to dissolve eventually precipitated crystals of the C polymorph. The C polymorph was obtained by rapid crystallization from pentane, which led mostly to the C polymorph. To transform eventually precipitated crystals of the B polymorph, the precipitate was annealed for 5–10 h at 62°C.

The polymorphic modification was checked by obtaining the X-ray diffraction patterns. Co radiation ($\lambda = 0.178$ nm) was used. The d_{003} long spacings observed were at $2\theta = 6.9$ and 7.6° for the B and C polymorph, respectively. The patterns observed always showed only negligible amounts of the undesired polymorph.

The heats of dissolution in decane (> 99%, Fluka), cyclohexane (> 99.5%, Fluka), methanol (> 99.6%, < 0.1% water, Prolabo) and butanone (> 99.5%, Merck) were obtained using a CRMT calorimeter. This is a revolving isothermal calorimeter with a Tian–Calvet thermopile. Such a calorimeter has the advantage, that the sample is at the same temperature before and after the experiment, thus effects due to differences in the heat capacities are eliminated. The calibration was achieved using Joule's effect.

The calorimeter has been described in detail by Coten et al. [3]. The measuring cell, as described by Barès [4], was used with only some minor modifications, see Fig. 1. The stearic acid was placed in the lower compartment and separated from the solvent by a steel platelet sealed with mercury. After thermal equilibrium was attained in the calorimeter, the cell was rotated within the calorimeter until complete mixing was achieved. Blank runs to assess the thermal effects of the rotations gave 0.29 ± 0.01 J ($n = 10$, where n is the number of measurements). The thermal effects of the actual runs were in the order of 10 J, so that good reproducibilities could be expected.

The reproducibility was estimated by measuring the heat of dissolution for the B polymorph at constant concentration ($c = 0.020$ mole l^{-1}) in decane:

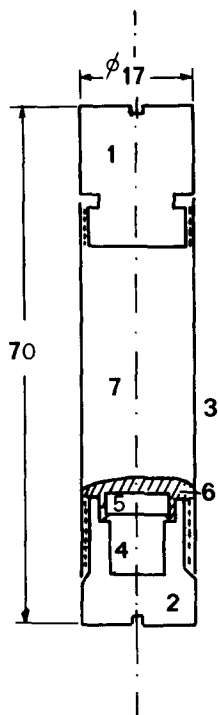


Fig. 1. Cross section of the cell used to measure the heats of dissolution. 1 and 2, Upper and lower teflon stopcock; 3, stainless steel cylinder; 4, sample compartment; 5, stainless steel platelet; 6, mercury seal; 7, solvent compartment (~ 7 ml).

$\Delta_d H_B = 70.6 \pm 0.6 \text{ kJ mole}^{-1} (n = 5)$. However, in subsequent measurements, such a limited scatter could not always be obtained. In addition, heat values which were too low were sometimes obtained: this may be explained by a partial penetration of the solvent into the sample compartment before the run.

The stearic acid used was as "crystallized" as well as ground. Except for slightly different dissolution kinetics, the results were the same.

All experiments were carried out at 30.8°C . At this temperature, sufficient quantities of stearic acid dissolve in all solvents ($> 2\%$ by weight), so that a good signal-to-noise ratio is obtained. On the other hand, the vapour pressures of the solvents are not too high as to give any serious problems (e.g. by evaporation into the dead space of the stearic acid compartment).

The heat of fusion was measured with the same calorimeter. For this, the temperature was increased at a rate of 10.9 K h^{-1} from 57 to 80°C and the heat flux into the sample (\dot{Q}) recorded, see Fig. 2. After subtraction of the flux into the empty cell, the integral with time gave the desired heat of fusion. The measurement was calibrated against the heat of fusion of diphenyl.

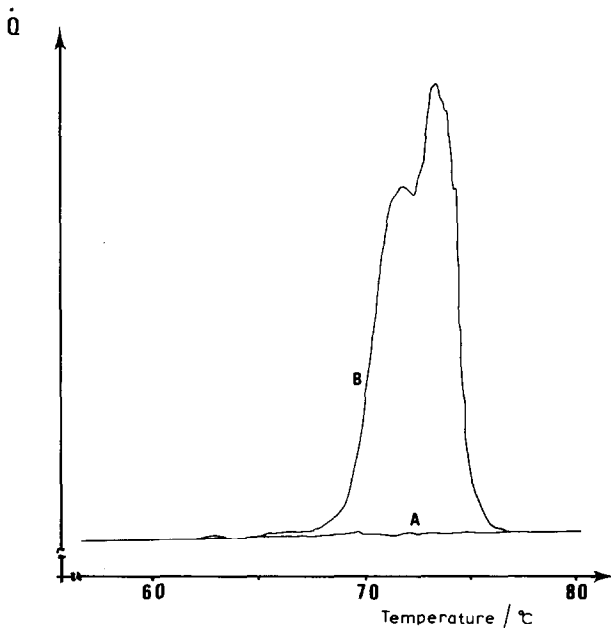


Fig. 2. Thermogram of the determination of the heat of fusion for stearic acid. The temperature was increased at a rate of 10.9 K h^{-1} . The baseline, A, was recorded with an empty cell, while B represents the actual run.

As all of these measurements are very time consuming (2–3 h), the number of measurements performed is relatively small.

RESULTS AND DISCUSSION

The heat of fusion, $\Delta_f H$, and the difference in heat capacities between the solid and the liquid, ΔC_p , are related to the heat of dissolution, $\Delta_d H$, by

$$\Delta_d H = \Delta_f H + \Delta C_p (T - T_f) + \Delta H^E \quad (1)$$

where the first two terms on the right hand side represent the ideal heat of dissolution and ΔH^E is the excess enthalpy. T and T_f are the temperatures of the solution and fusion, respectively. From the measurements of Singleton et al. [5] as well as Koga [6], one can deduce $\Delta C_p = 0$. For $\Delta_f H$, at least eight different publications give values between 57.7 and $70.2 \text{ kJ mole}^{-1}$ [6–10]. Direct determinations by DTA give 62.4 to $63.1 \text{ kJ mole}^{-1}$ [9,10]. Due to these uncertainties, we redetermined $\Delta_f H$ using the same calorimeter. We obtained $\Delta_f H = 62.6 \pm 0.2 \text{ kJ mole}^{-1}$ ($n = 2$). In these measurements, all thermal effects between 57 and 80°C were included. The results agree with the other direct determinations.

Stearic acid is dissociated in the melt at the melting point to 1.3% [11].

Taking a reasonable value for the heat of dissociation, see later, we find that $0.36 \text{ kJ mole}^{-1}$ have to be subtracted from $\Delta_f H$ to obtain the melting enthalpy of a stearic acid dimer.

The thermogram of the fusion, Fig. 2, shows peaks at 72 and 73°C. Both are at temperatures considerably higher than the melting points given in the literature, which range from 69.5 to 69.9°C [6,10–12]. This difference cannot be explained by impurities, but is probably due to a thermal lag between the bulk of the sample and the thermopile. We interpret the two peaks in the thermogram by a premelting or creation of disorder in the lattice before the actual melting. Such a premelting has already been described [6,8]. Berchiesi et al. [8] tried to assess the “true” melting enthalpy by cryoscopic measurements as $52.7 \text{ kJ mole}^{-1}$. If the first peak of our thermogram does indeed represent a premelting, the enthalpy will be $> 10 \text{ kJ mole}^{-1}$.

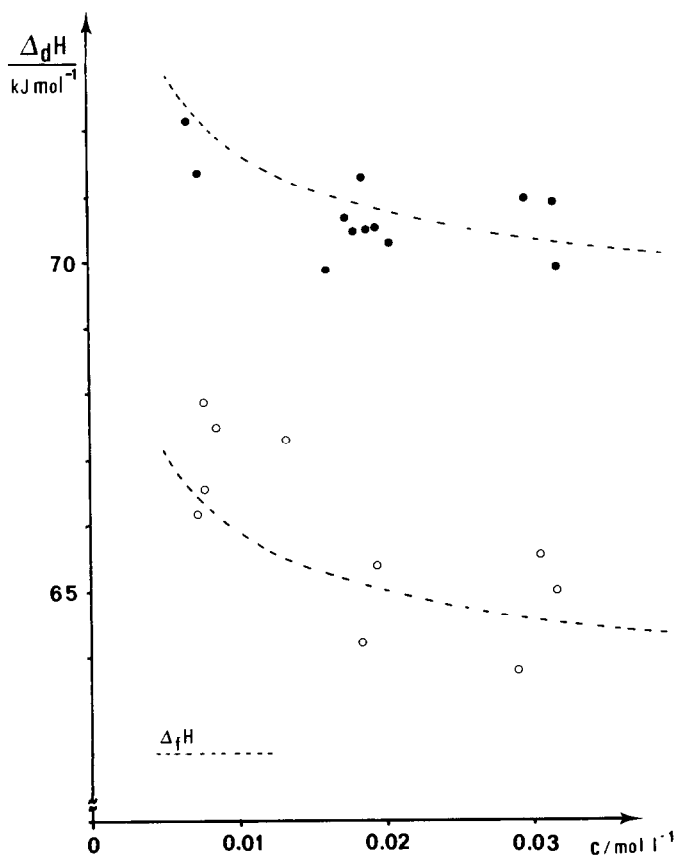


Fig. 3. Heats of dissolution of stearic acid in decane at 30.8°C as a function of concentration for (●) the B and (○) the C polymorph. The heat of fusion for the C polymorph is indicated. The traced lines give the heats deduced from the heat of fusion plus a partial dissociation [eqns. (4) and (5)].

In decane and methanol, we obtained the heat of dissolution as a function of concentration [$0.01 < c(\text{mole l}^{-1}) < 0.04$] for both polymorphs. For decane as solvent, a decrease of the heat of dissolution with increasing concentration can be seen, Fig. 3. For methanol as solvent, the heat of dissolution is constant within this concentration range. Secondly, we obtained a difference in the heat of dissolution between both polymorphs in both solvents independent of concentration of $\Delta_d H_B - \Delta_d H_C = 6.0 \pm 0.6 \text{ kJ mole}^{-1}$. This heat should equal the heat of polymorphic transformation in the solid state, for which Garti et al. [13] found values of 5.7 and 6.0 kJ mole⁻¹ by DTA measurements. The agreement is good.

The difference between the heat of dissolution and the heat of fusion ($\Delta_d H > \Delta_f H$) for decane as solvent cannot be explained by a heat of mixing, as, for example, given in the physical theory of solutions. Such a heat would (1) tend to zero for $c \rightarrow 0$ and (2) be constant in the relatively small concentration range investigated here if referred per mole of the solute. However, an entirely ideal solution is not to be expected either, as in the liquid dipole-dipole interactions of the charged COOH group still exist, while they are negligible in very dilute solutions. From potential calculations, the heat of breaking the dipoles in going from the solid to gaseous state is 1 kJ mole⁻¹ [14], which is small compared to $\Delta_f H$. The interactions of the aliphatic chain of the stearic acid with the decane should be even smaller due to the great similarities in structure.

We interpret the deviations in the heats of dissolution from the heat of fusion by a partial dissociation of the stearic acid dimer according to



with a dissociation constant K , such that

$$K = \frac{[\text{Sa}]^2}{[\text{Sa}_2]} \quad (3)$$

where $[\text{Sa}]$ and $[\text{Sa}_2]$ represent the stearic acid monomer and dimer concentrations, respectively. Such a dissociation has already been observed for stearic acid in non-polar solvents such as cyclohexane with $K = 3.5 \times 10^{-3}$ [15] at 80°C and benzene with $K = 22 \times 10^{-3}$ or 46×10^{-3} [15,16] at 80°C and $K = 1.8 \times 10^{-3}$ at 30°C [17] (the dimensions of K are mole l⁻¹).

We can separate the excess heat into two terms, one due to the dissociation, the other due to mixing

$$\Delta H^E = \frac{1}{2} \alpha \Delta_{\text{HB}} H + \Delta_m H \quad (4)$$

where α is the fraction of stearic acid dimers dissociated, which is related to K by

$$K = \frac{\alpha}{1 - \alpha} 2c \quad (5)$$

with c as the analytical monomer concentration. $\Delta_{\text{HB}} H$ is the heat of

dissociation of a stearic acid dimer, taken as 56 kJ mole^{-1} [11]. If we neglect any further thermal effects of mixing (i.e. assume an ideal solution), we may set $\Delta_m H = 0$. With $1 - \alpha \approx 1$, eqns. (4) and (5) lead to

$$K = 8c \left(\frac{\Delta H^E}{\Delta_{\text{HB}} H} \right)^2 \quad (6)$$

from which we can deduce $K = 0.263 \times 10^{-3} \text{ mole l}^{-1}$ at 31°C . However, the dispersion is quite high with 30 to 40%. We traced the curves obtained with this value and eqns. (4) and (5) in Fig. 3.

In methanol, the dependance of $\Delta_d H$ with concentration is negligible. The averaged heats of dissolution for the two polymorphs are: B, $81.3 \pm 0.7 \text{ kJ mole}^{-1}$ ($n = 7$); C, $75.4 \pm 1.6 \text{ kJ mole}^{-1}$ ($n = 12$). The higher dispersion of the values for the C polymorph compared to the B polymorph is striking. We propose that in methanol a complete dissociation is followed by a solvent-solute interaction via hydrogen bonds. The net heat effect should be positive, because the hydrogen bonds between two carboxylic groups are stronger than between a carboxylic group and an alcohol [18]. The experimental heat of dissolution is $\sim 13 \text{ kJ mole}^{-1}$ higher than the heat of fusion.

The heats of dissolution in cyclohexane and butanone were only determined for the C polymorph and at one intermediate concentration. They were intended only as supplementary material. At $c = 0.020 \text{ mole l}^{-1}$ we obtained for: cyclohexane, $71.7 \pm 0.3 \text{ kJ mole}^{-1}$ ($n = 3$); butanone, $74.0 \pm 0.8 \text{ kJ mole}^{-1}$ ($n = 3$). Here again, we explain the values higher than $\Delta_f H$ by a dissociation.

The dissociation in cyclohexane is only partial. Using eqn. (6), we obtain $K = 4.6 \times 10^{-3} \text{ mole l}^{-1}$, as compared to the literature value of 3.5×10^{-3} at 80°C . However, it is questionable, that stearic acid and cyclohexane form an ideal solution as assumed for decane above.

It was deduced from measurements of the excess volumes of the solutions, that the dissociation in butanone is complete [19]. The heat of dissociation is counterbalanced in part by a hydrogen bond formation with the solvent. This should be the same effect as for methanol as solvent and consequently both heats of dissolution are close (for methanol at the same concentration $\Delta_d H = 75.4 \text{ kJ mole}^{-1}$).

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