

ON PREMELTING OF THE C-FORM OF STEARIC ACID

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Some evidence is given for the presence of a solid phase just below the melting point of stearic acid. It is not certain whether the existence of this new phase is due to impurities or not.

Some work has been devoted to premelting phenomena of the stable C-form of stearic acid by means of NMR [1, 3], IR [1] and thermal analysis [4, 5]. Although the effect of impurities is not fully clarified, it seems safe to say that, at about ten degrees below the melting point, molecules begin to acquire a considerable amount of freedom and tend to disorder. Indeed, Berchiesi *et al.* [5] have hinted that premelting of stearic acid is due to the existence of a disordered phase just below the melting point, while some other members of fatty acids, such as margaric acid and pentadecanoic acid, have this disordered phase clearly separated from the melting point as evidenced in DTA curves [6]. On the other hand, Smit [7] has purified stearic acid carefully, and the melting curve he obtained on his sample was very sharp (the melting range from 69.5 to 69.6°). It is interesting to note, however, that in Smit's apparatus the sample was enclosed between two glass cylinders with a thickness of less than 0.04 cm and, as is well known for CCl₄ [10-12], glass surfaces can alter the relative stability of polymorphs.

During an attempt, by means of adiabatic calorimetry, to study irreversible transformations from other metastable forms of stearic acid to the stable C-form, a specimen of the C-form was prepared. With this sample in a copper container of volume of about 30 ml, some evidence was found to support the existence of another phase just below the melting point. Although it is not certain at this stage whether the existence of another phase is due to impurities or is intrinsic to stearic acid, it was felt worthwhile to present a preliminary report.

Experimental

An LKB 8700 reaction calorimeter was modified to become a conventional adiabatic calorimeter. The thermistor provided was used as the main temperature sensor and the resistance was measured by means of a Wheatstone bridge attached

to the system. The connection between the sensor and the bridge was via three wires. An unbalanced voltage was amplified with a Hewlett–Packard null-voltmeter and fed to a strip chart recorder. The thermistor was calibrated against a Pt-resistance thermometer (Lake Shore Cryogenics), which in turn was calibrated at the melting points of H_2O , $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, $\text{NaBr} \cdot 2 \text{H}_2\text{O}$ and naphthalene. Although the accuracy of calibration is not better than $\pm 0.1^\circ$, the use of the thermistor combined with the Wheatstone bridge gave a sensitivity of determination of temperature change to better than 0.01° . The general construction of the cell and the adiabatic shield was the same as that of Morrison *et al.* [11]. The adiabatic shield was surrounded by a radiation shield which, in turn, was suspended in a vacuum tight container. The container was immersed in an LKB 7600A Precision Thermostat, the temperature of which was controlled within $\pm 0.001^\circ$. The temperature difference between the cell and the adiabatic shield was monitored by three copper-constantan thermocouples in series and the voltage was amplified by a Hewlett–Packard pico-ammeter. The amplified signal activated the controller which controlled the temperature difference within $\pm 0.02^\circ$ of a desired set point. The temperature difference between the cell and the adiabatic shield could be set at will, and this facilitated a constant cooling or heating for a long period of time.

Stearic acid (BDH Pure) was purified by recrystallization from dry acetone (dried with K_2CO_3) three times. Although it is known to be difficult to separate fatty acid impurities by this method [9], it is the only feasible method to obtain a reasonably pure sample in a large quantity suitable for calorimetry. Care was taken so that no moisture contaminated the sample by handling it under a dry nitrogen atmosphere or by using a CaCl_2 drying tube when contact with the atmosphere was necessary. After decantation, the remaining acetone was evacuated through a cold trap. A product of fine flakes resulted. The melting point of this purified sample, measured on a conventional hot stage equipped with a magnifier was 69.4° , which is 0.2° lower than the published value. However, as the sample, was left unsealed, the melting point changed within 10 min to 69.0° and, after further 10 min, to 68.2° . As has been pointed out [3], this depression of the melting point can be ascribed to absorption of moisture. Even the initial sample of melting point 69.4° was probably not free from contamination by moisture, as it was inevitably exposed to the atmosphere when it was mounted on the hot stage.

The sample was recrystallized again from toluene (Analysed Reagent ACS, A and K Petro Chem. Ind.) under a dry atmosphere to produce forms other than the stable C-form, following the method of Bailey *et al.* [7]. The residual toluene was pumped off as before but, during the course of the evacuation, the vacuum was broken accidentally for half an hour or so, and contamination with moisture probably occurred. Evacuation was resumed and continued for 24 hours. The final sample was sealed into the cell made of copper in a dry nitrogen atmosphere. With this sample, a preliminary study on the transformations to the stable C-

form was carried out.* The sample was melted at the final stage of the study. As is well known [8], the solid formed from the melt is inevitably in *C*-form. This was confirmed by the IR spectrum taken at the end of the present study. The sample in the sealed cell was kept in a desiccator for two years and used for the present study.

Results and discussion

The measured heat capacities are plotted in Fig. 1. Thermal equilibration after an energy input was attained in less than 30 min except near the melting point where normally three to five hours was needed. Data from seven runs are included, each involving cooling from a variety of states; solid, liquid, incomplete melting of *C*-form, and C_α -form (see below). Rates of cooling varied widely, ranging from

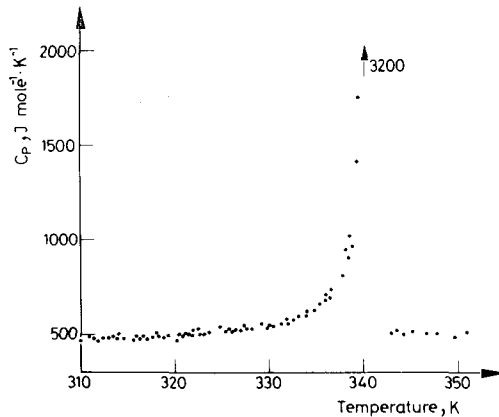


Fig. 1. Specific heat (C_p) of stearic acid

a few hours to 10 days to cool by 50°. The heat capacity was found to be independent of the prior thermal treatment which suggests that the stable *C*-form was always attained. The value of C_p starts to rise at about 330 K, similar to the pre-melting observed by DTA [6]. Alternatively this could suggest a second order transition at about 341 K. Figure 2 shows the curve of temperature *vs.* energy input. The melting point is 342.4 ± 0.1 K (69.2 ± 0.1) and the melting range is about

* Thermal anomalies were found [14] at 46°, 49° and 56°, the first corresponding to the transition from *B*-form to *C*-form and the third from *A*-form to *C*-form. The one at 46° was reproduced when the C_p measurement was repeated after cooling the sample which had not undergone melting. On the other hand, the separate study by means of IR showed that once the sample was heated at temperatures between 46° and the melting point, it changed to the *C*-form, and did not transform back to the original forms when it was cooled below 46°.

~ 1 K, indicating the presence of impurity. However, the plot of the temperature *vs.* the inverse of the fraction melted, assuming that there is only one melting process from the stable C-form to the liquid, did not give a straight line. The total energy of conversion from the stable C-form to the liquid calculated from Fig. 2

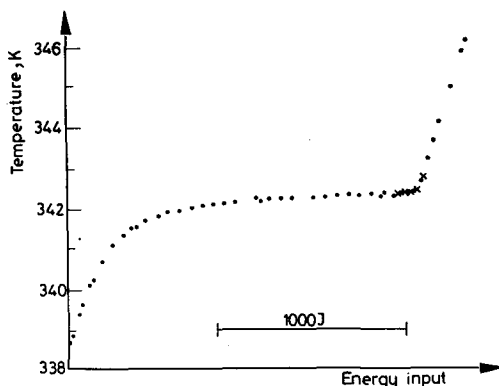


Fig. 2. Temperature *vs.* energy input in the course of melting

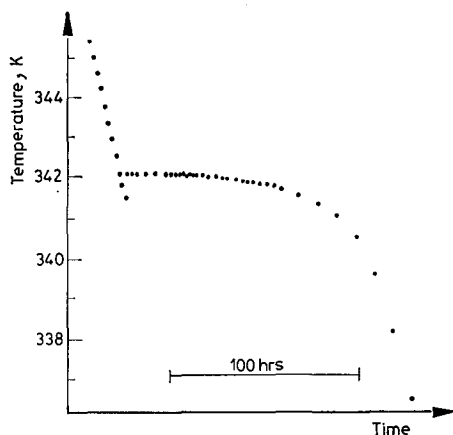


Fig. 3. Cooling curve

is 14.3 ± 0.3 kcal/mole. On the other hand, the slow cooling curve shown in Fig. 3 indicates that the freezing point is about 342.0 ± 0.1 K, i.e., about 0.4° lower than the melting point, suggesting two different solid phases. Typical heating curves are given in Fig. 4, which shows a smooth transition up to point A in the figure followed by superheating and melting. In one of the heating runs, the power was cut off at the first sign of melting and the system was allowed to equilibrate thermally. The equilibrium temperature attained was 342.4 ± 0.1 K, the same as the melt-

ing point obtained from the intermittent heating curve (Fig. 2). In one of the cooling runs from the melt, cooling was stopped after the first sign of freezing by restoring adiabatic conditions. After 3 hrs, which normally was a thermal equilibration time with two phases coexisting, the temperature reached 342.0 K, the same

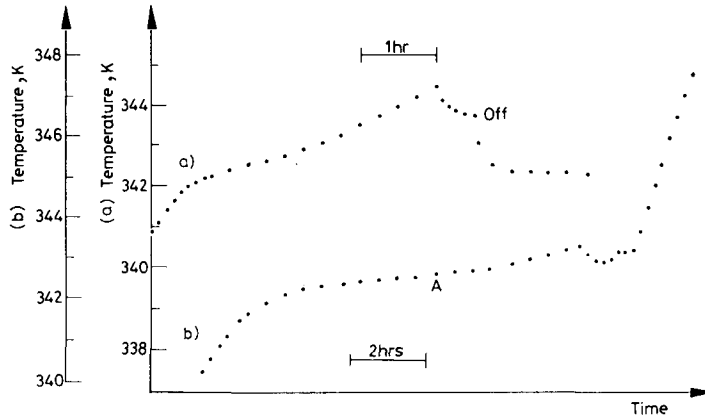


Fig. 4. Heating curves

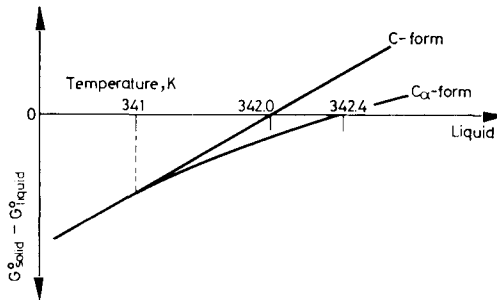


Fig. 5. Tentative phase diagram

as the freezing point obtained from the slow continuous cooling curve as seen in Fig. 3. The temperature, however, continued to drift upwards slowly and in 76 hrs it reached 342.4 K and stayed constant for further 8 hrs. Points after subsequent intermittent heatings fell on the curve of Fig. 2, these points being distinguished by crosses in the figure.

All of the above results seem to indicate the existence of another solid phase (called the C_α -form tentatively) and its relationship to the C -form and the liquid is sketched in Fig. 5. The change from the C -form to the C_α -form is of second or higher order. On heating, the C -form change smoothly to the C_α -form and to the liquid. On cooling the C -form is formed first with supercooling. The change from the C -form to the more stable C_α -form being evidently very slow (76 hrs), if cooling is faster than this time scale, the C_α -form is not realized. The change from C_α to

liquid may also be of second or higher order, since there is no apparent break corresponding to the beginning of this change in Fig. 2. However, the presence of the superheating shown in Fig. 4 might suggest that it is of first order. It is quite possible that impurities smeared the break in Fig. 2.

Thus, the argument by Berchiesi *et al.* that the premelting phenomena is due to the existence of another phase is tentatively supported. However, the possibility that the existence of the C_α -form is caused by impurities cannot be ruled out at this stage. Indeed, Mraw *et al.* [13] showed that impurities affect polymorphism in cesium nitrite. On the other hand, if the effect of glass surfaces prevented Smit [9] from observing premelting phenomena, the possibility of which still exists, the criterion for purity needs to be explored further.

In any case, a technique to purify stearic acid in large quantity needs to be developed.

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RÉSUMÉ — On donne plusieurs preuves de la présence d'une phase solide juste au-dessous du point de fusion de l'acide stéarique. Il n'est pas certain que l'existence de cette phase nouvelle soit due à des impuretés ou non.

ZUSAMMENFASSUNG — Einige Beweise zur Gegenwart einer Festphase knapp unterhalb des Schmelzpunktes der Stearinsäure werden gegeben. Es ist nicht geklärt ob das Vorhandensein dieser neuen Phase auf Verunreinigungen zurückzuführen ist oder nicht.

Резюме — Представлены некоторые доказательства наличия твердой фазы для стеариновой кислоты ниже ее точки плавления. Только не определено, что существование этой новой фазы обусловлено примесями или нет.