DETERMINATION OF THE COMPOSITION OF MIXTURES OF FATTY ACID POLYMORPHS BY DTA

NISSIM GARTI, SARA SARIG and EDNA WELLNER

Casali Institute of Applied Chemistry, School of Applied Science and Technology, Hebrew University of Jersualem, Jerusalem (Israel)

(Received 27 August 1979)

ABSTRACT

The effect of various solvents on the crystal structure of pure stearic acid crystallized from them was studied using X-ray and differential thermal analysis. The latent heat of the phase transition, ΔH_t, was measured for the two well-defined forms B and C.

X-Ray diffractograms are the means for the identification of crystal modifications. However, only qualitative information about the composition present in the mixture can be inferred from the relative peak intensities.

Differential thermal analysis of the phase transitions at $54°C$ (for B) and $64°C$ (for A) furnishes quantitative data for each component present in the mixture.

Values of 0 and 4.9 cal g^{-1} for the phase transition enthalpies were measured for the pure C form and B form, respectively. Intermediate values were found for mixtures of C and B.

The interplay between the crystallization conditions (type of solvent, cooling rate and flow regime) dictates the formation of various crystal structure modifications

INTRODUCTION

Many long chain compounds exist in more than one crystalline form. These forms have different lattice energies and sometimes display different physical properties. This phenomenon, known as polymorphism, is of both academic and practical interest in the field of research and production of fats, since the understanding of polymorphic changes is essential for the satisfactory blending and tempering of those fats which must maintain a certain physical appearance during preparation and storage [1,2]. Problems of graininess in margarine and blooming in chocolate are related to polymorphic changes [3].

Fatty acids are used as model substances for the study of polymorphism of fats because their behavior is analogous in many respects to that of fats and they crystallize easily in well-defined polymorphic forms.

The polymorphism of fatty acids has been studied most extensively using X-ray diffraction, infrared spectroscopy, dilatometry and, to some extent, their behavior during cooling and heating was followed up [2].

Investigators using X-ray and infrared techniques have shown that the even-numbered *n*-saturated acids exist in three forms (A, B, and C) [4—7].

Another form (named E) was detected using infrared spectroscopy [8—11]. It was demonstrated that the C form is the most stable thermodynamically and may be obtained by solidification of the melt and sometimes by crystallization from a polar solvent [7].

Crystallization from a non-polar solvent usually gives either the A form or the B and C forms together. It is well established that, when heated, A and B forms are transformed irreversibly to the C form before melting so that it is the melting point of the C form which is always measured [6].

Specific heats, heats of crystallization, and heats of transition of the long chain fatty acids were measured by Garner et al. over a period of ten years [9,10]. Their results summarized efforts in measuring those values by old techniques.

Bailey et al. [11] ascribed the nature of fatty acid crystals to the temperature—concentration characteristics in their formation regardless of any possible effect of the solvent. In general, mixtures of B and C were said to be formed between 20 and 30°C.

The stability ranges of the different modifications of the normal chained fatty acids were studied by X-ray diffraction by Von Sydow and co-workers. Phase transitions at 46°C and 54°C were determined for forms B and A, respectively [6,7].

No attempts have been made to evaluate these phase transitions quantitatively. Studies carried out by our group showed that the nature of the solvent, the cooling rate and the presence of impurities can affect the nature of the crystalline modification of the fatty acid obtained and, in many cases, several modifications are present in a mixture [12].

Phase transition energy changes can be easily measured using DTA techniques. From these values, the percentage of each modification present in the mixture can be calculated. This study compared the composition determinations of mixtures of polymorphs carried out by X-ray and DTA for various stearic acid samples crystallized from different solvents under various conditions.

EXPERIMENTAL

Materials

Stearic acid from BDH chemicals was purchased at >99.5% purity and was further purified by repeated crystallization from ethanol. The absence of impurities, except for palmitic acid (<1%), was established by gas chromatography. The melting point was 69.5°C and elemental analysis showed C = 76.30% (calcd. 76.06%) and H = 12.60% (calcd. 12.68%). The fatty acid was in the C form according to X-ray measurements.

The solvents for crystallization were spectroscopic grade purchased from Malinkrodt and Baker and were used without further purification.

Crystallization techniques

All the experiments were carried out in a thermostatic bath with controlled cooling profile. Crystallization temperatures were in the 20—30°C range.

Analytical methods

Simultaneous DTA, TG, and DTG determinations were carried out on a Mettler thermoanalyzer under a controlled dry nitrogen flow of $5 \, l \, h^{-1}$. The samples were in the range of 50—70 mg and the heating rate was $2°C \, min^{-1}$. The DTA sensitivity was 50 μV f.s.d.

The latent heat of melting (ΔH_m) and of polymorphic transition (ΔH_t) were calculated from DTA peak areas. The calibration for the heat of transition (which occurs in the range 54—65°C) was carried out with lauric acid which has a melting point at 40—43°C and a latent heat of melting of 43.72 cal g^{-1}. The heat of fusion of indium was also used as a reference (6.8 cal g^{-1}). X-Ray measurements were carried out on carefully ground powder with a Philips diffractometer using Cu radiation and Ni filter. Diffraction analysis was repeated several times using samples crystallized from various solvents under different conditions.

RESULTS

The X-ray diffraction patterns of pure C form and pure B form compared with a mixture of both, are illustrated in Fig. 1. The marked differences between the modifications are in the area of $2\theta = 5—1°$. The DTA curves for phase transition and melting of stearic acid crystallized as pure C form (from hexane) and of pure B form (from benzene) are shown in Fig. 2. The DTA curves of stearic acid crystallized from hexane at 0.03°C min^{-1} and at 1.0°C min^{-1} are demonstrated in Fig. 3.

Table 1 summarizes the heats of transition of stearic acid crystals precipitated from four different solvents in quiescent and stirred systems cooled at the rate of ca. 0.03°C min^{-1}. In addition, an estimation of the relative amounts of the C and B forms as indicated by the peak intensities characteristic to their respective X-ray diffractograms are listed.

Pure C form was obtained at the slow cooling rate from a quiescent hexane solution. No heat of transition was detected for these crystals ($\Delta H_t = 0$) confirming that they are the stable C form. The pure B form was also obtained from hexane solution but with different flow regime, i.e. with constant stirring. In this case, a significant latent heat of 4.9 cal g^{-1} accompanied the phase transition of the crystals from B to C.

The interesting cases are those in which it is difficult to estimate the relative amounts of B and C in mixtures. The results according to X-ray diffractograms are given for crystals obtained from stirred benzene solution as B > C and from stirred acetone solution where C form is clearly dominant as C >>> B. The heats of transition were $\Delta H_t = 1.7$ cal g^{-1} and $\Delta H_t = 0$.
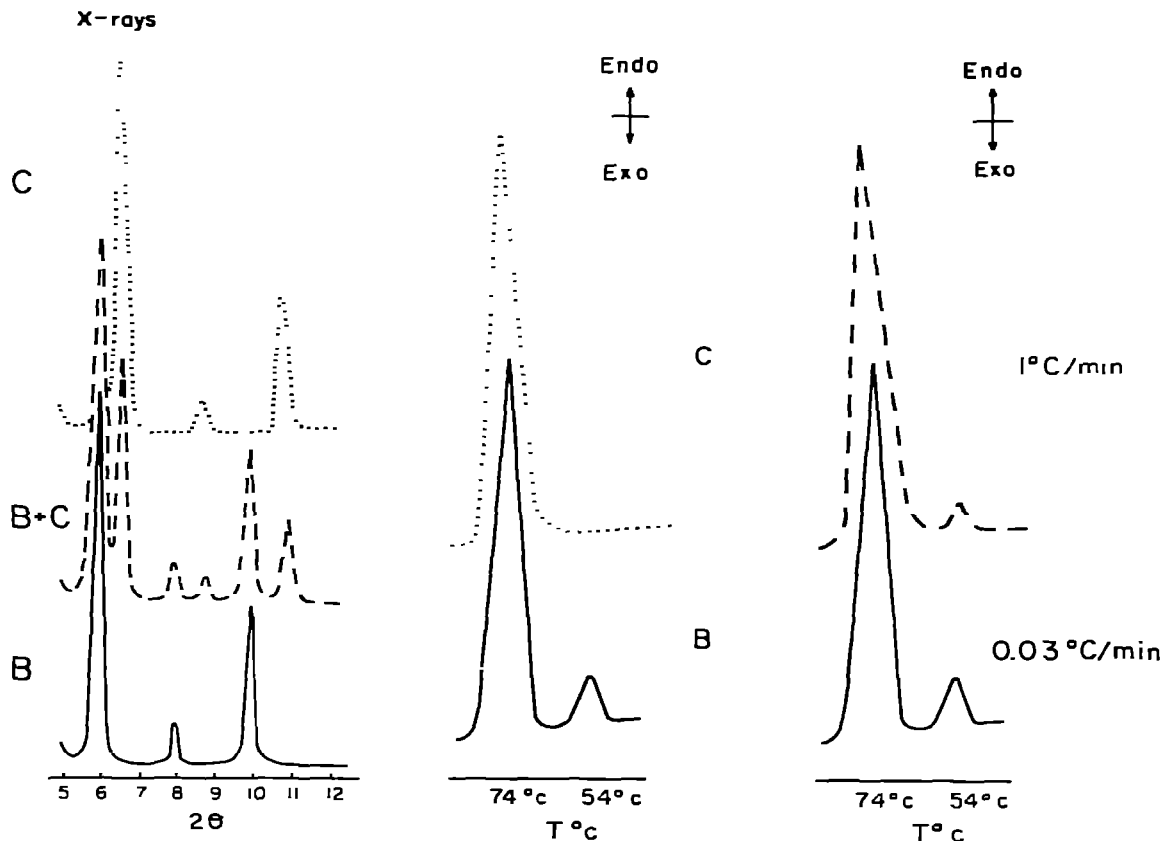
Fig. 1. The X-ray diffraction pattern spectrum of pure C form compared with pure B form and a mixture of both forms.

Fig. 2. DTA curves of phase transition and melting of stearic acid crystallized as pure C form and as pure B form.

Fig. 3. DTA curves of phase transition and melting of stearic acid crystallized from hexane at $0.03°C$ min^{-1} and $1.0°C$ min^{-1} in stirred systems.

TABLE 1

Heat of phase transition (at $54°C$) of pure stearic acid crystallized from various solvents in quiescent and stirred systems at a cooling rate of ca. $0.03°C$ min^{-1}

No.	Solvent	Condition of crystallization	T_c (°C)	ΔH_t (cal g^{-1})	X-Rays
1	Hexane	Quiescent	30.5	0	C
2	Hexane	Stirred	30.8	4.9	B
3	Benzene	Quiescent	26.7	3.2	B
4	Benzene	Stirred	28.3	1.7	B > C
5	Acetone	Quiescent	26.2	0	C >> B
6	Acetone	Stirred	27.0	0	C >>> B
7	Ethanol	Quiescent	24.9	2.6	B > C
8	Ethanol	Stirred	25.7	3.6	B

respectively. It therefore seems established that whenever B form is present in a mixture, a detectable heat accompanies the transition to C, falling short of ~5 cal g^{-1} when C is also present. When the amount of B is very small compared with C, it may be undetectable by the heat effect.

Pure B form was obtained from a quiescent benzene solution, according to X-ray diffractogram (Table 1). However, the heat of transition was only 3.2 cal g^{-1} indicating some admixture of C. When the heat was slightly lower, 2.6 cal g^{-1} as for the crystals obtained from a quiescent ethanol solution, the amount of C was large enough to appear in the X-ray diffractogram. As for the crystals from the quiescent benzene solution, the only indication of the presence of an admixture of C was the low heat of transition.

It is clear that the DTA determination is more exact with respect to admixture detection than the X-ray diffractogram. Mixtures are notoriously non-homogeneous and the relative amounts of components detected depend strongly upon sampling. The samples used for DTA are significantly larger than those used in X-ray analysis thus improving the chances of obtaining more realistic results.

Additional evidence to this effect is given in Table 2. It is interesting to note that an increase in cooling rate, which increases the supersaturation and enhances the nucleation rate, causes changes in the mixture composition which in some instances is startling. For instance, with high cooling rate the B form was predominantly obtained from the quiescent hexane solution, whereas at a cooling rate of 0.03°C min^{-1}, pure C was obtained. The crystals (sample 1, Table 2) had a heat of transition of 2.8 cal g^{-1}. In fact, the crystals from mixtures characterized by the ratio B >> C all had heats of transition of about the same value (samples 1—3, Table 2). A slightly higher value of 3.14 cal g^{-1} corresponded to a mixture with only a very small amount of C (sample 4, Table 2). However, the conformity cannot be taken as absolute. When the values of transition heat were 2.7—3.0 cal g^{-1} (samples 7 and 8, Table 2), the X-ray diffractogram did not show the presence of C. This phenomenon is connected with crystals precipitated from ethanol (cf. Table 1).

TABLE 2

Heat of transition of pure stearic acid crystallized from various solvents at a cooling rate of 1°C min^{-1}

No.	Solvent	Conditions of crystallization	T_c (°C)	ΔH_t (cal g^{-1})	X-Rays
1	Hexane	Quiescent	23.8	2.8	B >> C
2	Hexane	Stirred	27.7	2.7	B >> C
3	Benzene	Quiescent	24.8	2.8	B >> C
4	Benzene	Stirred	26.5	3.14	B >>> C
5	Acetone	Quiescent	24.2	0	C > B
6	Acetone	Stirred	26.3	<1	C > B
7	Ethanol	Quiescent	19.3	2.7	B
8	Ethanol	Stirred	23.1	3.0	B

The mixture composition of stearic acid polymorphs is the outcome of a complex interplay of many parameters including solvent—solute interaction, rate of supersaturation formation, flow regime, temperature, etc. In some instances, pure forms crystallize but in many experimental conditions, a mixture of polymorphs is formed. No comprehensive theory has yet been proposed by the numerous investigators of the crystallization of fatty acids as to the effect of crystallization conditions on the nature of the crystals. Part of the difficulty may have stemmed from the inaccurate data concerning the crystallographic forms obtained and analyzed by the non-quantitative X-ray technique. The combination of DTA and X-ray may contribute to a more accurate evaluation of the composition of fatty acid crystal mixtures thus facilitating the understanding of the conditions of their formation.

REFERENCES

1 D. Chapman, The Structure of Lipids, Methuen, London, 1965. F.D. Gunstone, An Introduction to the Chemistry and Biochemistry of Fatty Acids and their Glycerides, Chapman and Hall, London. 1967.
2 K.S. Markley, Fatty Acids, Part 1, Interscience, New York, 1947, 2nd edn., p 93.
3 N. Krog and B. Nybo Jensen, Grindsted Products Technical Paper TP 22-1e, 1970.
4 D.J. Chapman, J. Chem. Soc., (1962) 2310.
5 F.F. Bentley, M.T. Ryan and J.E. Katon, Spectrochim. Acta, 20 (1964) 685.
6 E. Stenhagen and E. Von Sydow., Ark. Kemi, 6 (1953) 309.
7 E. Von Sydow, Ark. Kemi, 9 (1956) 231.
8 R.F. Holland and J. Rud Nielsen, Acta Crystallogr. 16 (1963) 902.
9 W.E. Garner, F.C. Madden and J.E. Rushbrooke, J. Chem Soc., (1926) 2491.
10 A.M. King and W.E. Garner, J. Chem. Soc., (1936) 1368, 1372.
11 A.V. Bailey, D. Mitcham, R.A. Pittman and G. Sumrell. J. Am. Oil Chem. Soc., 49 (1972) 419.
12 N. Garti, E. Wellner and S. Sarig, in preparation.