Crystal Structures of Binary Systems of Saturated Fatty Acids

E. FREDE and **D. PRECHT**, Institute for Physics, Bundesanstalt für Milchforschung Kiel, Federal Republic of Germany

ABSTRACT

Data on crystal lattices of 13 different mixtures of the system palmitic acid:stearic acid (C_{16}/C_{18}) could be obtained by means of X-ray and electron diffraction. The modification occurring in all concentrations was found to be in conformity with the known γ_4- or C-form of the pure components. It is characterized by the fact that, in mixtures with 95-60 mol % stearic acid, the shorter chained palmitic acid molecules may be incorporated in the crystal lattice of pure stearic acid without dimension c of the unit cell being changed. In concentration ranges of 50-20% C_{18}-molecules, one form of mixture which proves to be stable is characterized by constancy of nearly all unit cell parameters of various mixture ratios. From SP10 to SP0, the lattice constants of pure palmitic acid are mainly obtained. The occurrence of C_{18}-molecules of up to 10% in the unit cell of palmitic acid results in a slight decrease of the angle β by 1-2° and an enlargement of the distance to neighbored molecules.

INTRODUCTION

Long chain organic compounds such as paraffins, fatty acids, glycerides, and fatty alcohols are present in many natural and industrially produced substances; they occur in large numbers and in most complicated mixtures. The molecular arrangement of the different mixture components to each other essentially determines the consistency of a substance, as, for instance, its melting and solidification behavior. Knowledge of the microstructure of such complex systems is therefore of great importance from the points of view of science and technology. So far, however, it was possible only to a very limited extent to obtain precise data of crystal structures of binary mixtures from homologs of unbranched chains (paraffins, fatty alcohols, fatty acids). Only for one mixture concentration (1:1) of the binary system stearic acid:palmitic acid were unit cell parameters given by Degermann and von Sydow (1).

It is the aim of this study to find out, by the example of the binary system stearic acid:palmitic acid, to what extent unbranched fatty acids, differing in their molecular length by two CH_2-groups, may be able to form mixed crystals and in which modification possible mixture forms may occur. In the case of mixed crystal formation, it is of special importance to determine exactly, by means of X-ray and electron diffraction, all unit cell parameters and the theoretical densities in dependence on the concentration of the mixture and to consider the molecular arrangement of the forms of mixtures obtained.

EXPERIMENTAL PROCEDURES

Palmitic and stearic acids (Fluka AG, Buchs, Switzerland; analytical grade "purissimum," $\geqslant 99\%$) were mechanically mixed in the solid state in 13 molar ratios 0:100, 5:95, 10:90. . . 95:5 and 100:0 (abbreviated SP0, SP5 . . . corresponding to 0%, 5%,. . . stearic acid) and finely ground by means of a pestle to obtain a mixture as homogenous as possible. A Geiger-Müller counter X-ray diffractometer, manufactured by Philips, was used to take the X-ray patterns. Cu-Kα-irradiation ($\lambda = 1.541838$ Å) was used in the measurements. Five preparations were made of every mixture under exactly the same conditions. For this, the samples were melted in a copper vessel at a temperature of 100 C on a heater-block rinsed with a thermostatic liquid and subsequently chilled to 10 C on a cooler block. The surfaces of preparation holders were ground in to exactly $\pm 5\ \mu$ to secure precise measurements of X-ray diffraction lines.

An angular velocity of 1°/min was sufficient for recording the survey X-ray patterns of the various mixtures. For precise measurements, the crystal reflections used for a unit cell determination were individually recorded for every mixture with an angular velocity of 1/8°/min and with the optimum range of apertures, time constants, and mean value adjustments of the pulse rate.

An electron microscope EM 301, manufactured by Philips, was used to take the electron diffraction patterns. Diffraction patterns could be obtained from single crystals (Laue patterns) as well as from polycrystalline material (Debye-Scherrer rings) under different angles of tilt. Petroleum ether 0.01% solutions were prepared from the sample made for X-ray diffraction and finely atomized in small amounts in an ultrasonic atomizer at 3 MHz. Thus, the rapidly vaporizing solvent allowed small single crystals to grow from the droplets.

The preparation holders consisted of fine copper grids with a diameter of 3 mm, the surface of which was overlaid with a thin carbon-damped carrier film of Formvar-material.

In addition to diffraction without image-producing lenses by means of a so-called high resolution diffraction unit, single crystal diagrams were also produced by means of selected area diffraction (5-10 μ condensor-II-apertures). Since fatty acid crystals are extremely sensitive to thermic treatment, minimum density of beam current had to be used so that the central beam spot was hardly perceptible on the screen. In order to visualize the diffraction patterns, they were reproduced on a monitor by means of a special TV display and image intensifying system. The choice of extremely sensitive photographic material, including an optimum developer, proved to be of importance, too.

TlCl was used as the calibration substance.

RESULTS

Description of X-Ray Diffraction Patterns

Apart from pure palmitic acid, all mixtures were exclusively present in the γ_4-form (nomenclature according to Precht [2]). This modification is in agreement with the C-form of Vand et al. [3]. SP0 did not only show the presence of the γ_4-form but also the β_2-modification (B-form of Larsson and von Sydow [4]). However, it was possible to obtain diagrams of the unmelted substance of the pure γ_4-modification for evaluation.

The γ_4-modification is characterized by short spacings at $2\theta = 21.5°$ ($110, 1\bar{1}0$-line), 24° ($200, \bar{2}00$), 20.2° ($\bar{1}\bar{1}2$), as well as by long spacings at $2\theta = 6.64°$ (003-line) corresponding with pure stearic acid and at 7.42° (003) for SP0.

The intensities of long spacings decrease from both ends of the mixture series to middle concentrations, namely, slowly and continuously on the longer chain side, while on the other end an abrupt intensity decrease is already observed at SP5.

The 003-reflections show a relatively broad profile of the lines between SP60 and SP5. The long spacings with Miller index of $\ell > 3$ are fully extinguished except in pure substances. The 110- and $\bar{1}\bar{1}2$-lines exhibit strong intensities in all mixtures, while the 200-reflections are remarkably smaller between SP50 and SP5 and have a broad profile in middle concentrations.

There is a striking constancy of the 020-subcell reflection at $2\theta = 36^\circ$ in all diagrams. High intensity of the $\bar{4}0$ (2+N)-lines of SP0, 5, 10, 80, 90, 95, and 100 is observed around $2\theta = 41.3^\circ$. N means the number of carbon atoms of a molecule of the respective fatty acid.

The position of the 001-reflections within the concentration ranges SP100-SP60, SP50-SP20, and SP10-SP0 proves to be relatively constant. There are only some variations of the lattice plane distances which are below 1 Å.

On the shorter chain side of the 003-lines of SP60 of some preparations, an additional line of weak intensity is observed which may be attributed to a middle form of mixture.

Description of the Electron Diffraction Patterns

Laue- and Debye-Scherrer patterns were taken by the electron microscope of the mixtures from SP30 to SP70. Figure 1 shows a Laue-pattern representing part of the 611-plane of the reciprocal lattice.

The extinctions of the $h0\ell$-reflections where h is odd correspond to space group C_{2h}^5-$P2_1/a$ described by Vand et al. (3) for the γ_4-modification of pure lauric acid.

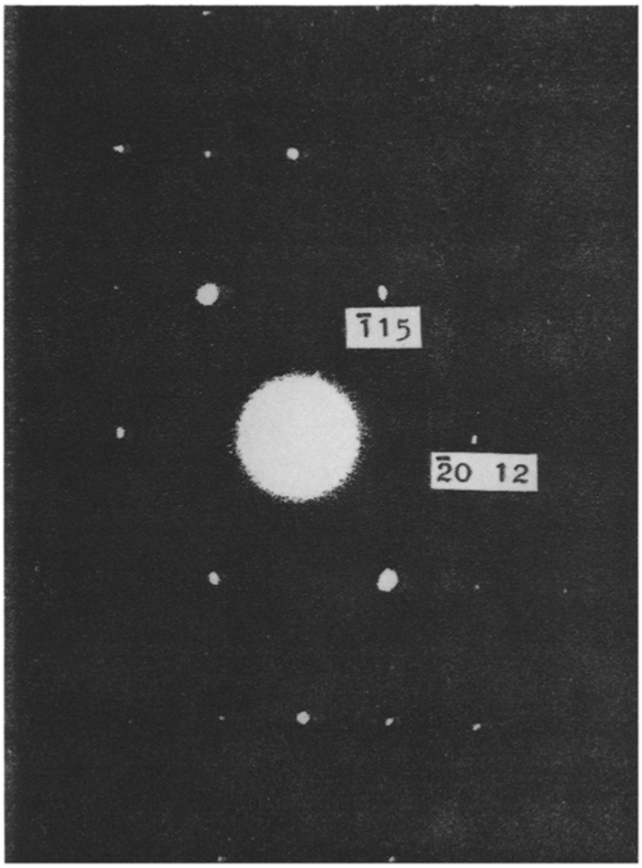

FIG. 1. Single crystal diffraction pattern of the γ_4-modification of the mixture SP70. Part of the 611-plane of the reciprocal lattice.

Evaluation

The various modifications and the index combinations of the lines in different X-ray patterns were determined, among others, by means of research results obtained by Larsson and von Sydow (4) on the β_2-form of stearic acid (C_{18}) and by Vand et al. (3) as well as by Malta et al. (5) on the γ_4-form of lauric acid (C_{12}) and stearic acid (C_{18}). The atomic coordinates of C_{16} and C_{18} could be calculated proceeding from C_{18} and under the inclusion of the fact that the molecules are somewhat bent. The relative intensities could be determined therefrom by means of a Fourier analysis.

The atomic coordinates of the β_2-forms of stearic and palmitic acid could be calculated from the relative y- and z-values of von Sydow (6) and from the x-values of a transformed β_2-form of Larsson and von Sydow (4). As previously mentioned, the intensities found from all these studies and the known unit cell parameters of the pure substances have shown the X-ray and electron diffraction patterns of the different mixtures to contain reflections exclusively of the monoclinic γ_4-form. Like the β'-modification of triglycerides (Buchheim [7]) which prevailingly occurs in trilaurin:trimyristin fatty mixtures (Frede and Precht, unpublished data), the γ_4-form of pure fatty acids possesses the orthorhombic subcell with every second chain plane perpendicular to the others as described for paraffins by Bunn (8) and Vainshtein/Pinsker (9).

DISCUSSION

The electron and X-ray diffractometric studies have shown the binary system stearic acid:palmitic acid not to decompose into its components during crystallization under the given experimental conditions. However, whether two phases of similar structure develop at middle concentration, as concluded by Slagle and Ott (10) from solidification curves, cannot be excluded for the reason of line expansions observed in the X-ray diffraction pattern between SP60 and SP5. Since the evaluation of the electron diffraction patterns gave identical unit cell parameters in the respective cases, it appears unlikely that a decomposition takes place in two phases with our method of preparation. Line expansions, as well as lacking long spacings of higher order, rather indicate a disturbed crystal arrangement with many lattice defects. The cross-sections $Q = ab \cdot \sin\beta$ of the mixtures SP5 to SP70 show values which are higher than those of the pure components. Lattice defects are indicated also by this lateral expansion of the unit cell. It appears understandable that, especially on the shorter chain end of the mixture series, a shortening of C_{18}-molecules provoked by defects (e.g., kinks or double kinks according to Pechhold et al. [11]) produces an expansion in vertical direction towards the chain axis.

That homologous isomorphism does not exactly exist in pure fatty acids is expressed in Table I by the fact that the unit cell of the longer chain component has a smaller cross-section, i.e., the molecules are packed closer. The closer packing mainly consists of a shortening of the subcell dimension b_s by 0.04 Å. Valid for b_s is $b_s \approx a \sin\tau$, with τ as the angle between the molecular chain projected on the ac-plane and the a-axis. For C_{18}, τ is $183.5^\circ - \beta$ according to Malta et al. (5); assuming that there is a comparative relation for C_{16}, the subcell dimensions b_s for the various mixtures could be given in Table I. Particularly striking is the abrupt increase of this parameter from SP0 to SP5. Also in this case, one can proceed from considerations similar to those which have led to the explanation of the varying unit cell cross-sections. On the other hand, dimension b and, with this, subcell parameter a_s remain nearly constant with 4.97 Å.

These results appear understandable if proceeding from the fact that the minimum distances of neighbored parallel carbon chains are around 4.97 Å and the chains for C_{18} and C_{16} are arranged almost vertically to each other around

TABLE I

Experimentally Determined Lattice Parameters of SP-Mixtures and Densities Calculated Therefrom

SP	a[Å]	b = a_s[Å]	c[Å]	β[°]	Q[Å^2]	ρ[g/cm^3]	a·sin β[Å]	c·sin β[Å]	b_s[Å]
100	9.41	4.97	51.04	128.51	36.58	1.001	7.36	39.94	7.71
95	9.40	4.97	50.96	128.4	36.63	1.007	7.37	39.94	7.71
90	9.42	4.97	51.03	128.5	36.63	1.001	7.37	39.94	7.72
80	9.42	4.97	50.89	128.3	36.73	0.991	7.39	39.94	7.74
70	9.44	4.97	50.75	128.0	37.10	0.971	7.45	40.00	7.78
60	9.45	4.97	50.77	127.8	37.13	0.963	7.47	40.12	7.81
50	9.43	4.97	48.7	127.0	37.42	1.006	7.53	38.91	7.86
40	9.38	4.97	47.9	127.0	37.23	0.996	7.49	38.27	7.82
30	9.37	4.97	48.3	127.0	37.18	0.978	7.48	38.54	7.81
20	9.37	4.97	47.9	127.0	37.18	0.975	7.48	38.29	7.81
10	9.34	4.98	45.81	126.9	37.20	1.010	7.47	36.63	7.80
5	9.48	4.98	45.91	128.1	37.15	1.004	7.46	36.13	7.80
0	9.49	4.98	45.85	128.78	36.85	1.008	7.40	35.74	7.75

4.59 Å. If the lattice defects occurring in the mixtures mainly consist of chain shortening, as for instance by the formation of kinks, it may be expected that in larger crystal ranges every second chain in the 110-direction does not continue to be perpendicular to the others. An expansion towards 100-direction would be the consequence, i.e., an enlargement of b_s and, with this, an approach to hexagonal chain packing (b_s = 8.61 Å), in which all distances of neighbored carbon chains are around 4.97 Å.

Parameter c varies only very slightly within concentration ranges of SP100 to SP60 and SP10 to SP0, being around 51 Å for pure stearic acid and around 45.9 Å for pure palmitic acid. The middle concentration range between SP50 and SP20 is characterized by the constancy of nearly all lattice parameters. As the average unit cell it may be stated:

$$a = 9.39,\ b = 4.97,\ c = 48.2\ \text{Å},\ \text{and}\ \beta = 127^\circ$$

The value of c is about the arithmetic mean of the corresponding dimensions of the pure components.

As to our results, it may be said that there are three characteristic concentration ranges in which there is the approximate unit cell of C_{18} between SP100 and SP60, an intermediate cell between SP50 and SP20, and the parameters of C_{16} between SP10 and SP0.

The occurring forms of the mixtures are characterized by the fact that in mixtures with 95-60 mol % stearic acid the shorter chain palmitic acid molecules may be incorporated in the crystal lattice of pure stearic acid without the unit cell parameters being changed essentially. On the other hand, the occurrence of up to 10% C_{18}-molecules in the crystal lattice of palmitic acid involves only a slight expansion of the unit cell cross-section or of b_s. Within this range the unit cell of C_{16} proved to be constant. The development of the mixed form in the range of SP50 to SP20 may perhaps be understood in the assumption that, during the process of crystallization, double molecules are formed with mathematically calculable probability from two stearic acid molecules, from two palmitic acid molecules, and from one stearic and one palmitic acid molecule. Model calculations for this are under preparation.

Degermann and von Sydow (1) came to the result that an "average" unit cell is present at SP50 which exclusively contains SP-molecules (space group $P2_1$). Based on our studies, however, it cannot be excluded that short and long chain molecules are distributed statistically. All single crystal patterns have shown extinctions of $0k0$- and $h0\ell$-reflections with odd h and k. This may eventually point to space group $P2_1/a$.

ACKNOWLEDGMENTS

The authors are indebted to Prof. Dr. E. Knoop, Director of the Institute for Physics of the Federal Dairy Research Center Kiel, for numerous discussions. Thanks are also due to Deutsche Forschungsgemeinschaft for making available the equipment required (X-ray diffractometer and electron microscope) in the experimental studies.

REFERENCES

1. Degermann, G., and E. von Sydow, Acta Chem. Scand. 12:1176 (1958).
2. Precht, D., Kieler Milchwirtsch. Forschungsber. 26:221 (1974).
3. Vand, V., W.M. Morley, and T.R. Lomer, Acta Crystallogr. 4:324 (1961).
4. Larsson, K., and E. von Sydow, Acta Chem. Scand. 20:1203 (1966).
5. Malta, V., C. Giancarlo, Z. Roberto, and A.F. Martelli, J. Chem. Soc. (B) 548 (1971).
6. von Sydow, E., Acta Crystallogr. 8:557 (1955).
7. Buchheim, W., Kieler Milchwirtsch. Forschungsber. 22:3 (1970).
8. Bunn, C.W., Trans. Faraday Soc. 35:482 (1939).
9. Vainshtein, B.K., and Z.G. Pinsker, Tr. Inst. Kristallogr. Akad. Nauk. SSR 7:163 (1951).
10. Slagle, F.B., and E.J. Ott, J. Am. Chem. Soc. 55:4404 (1933).
11. Pechhold, W., S. Blasenbrey, and S. Woerner, Kolloid-Z. Z. Poly. 189:14 (1963).

[Received June 4, 1976]