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An X-Ray Investigation of the Binary System Stearic Acid—Palmitic Acid

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The molecular arrangement for the 1:1 compound between stearic (S) and palmitic (P) acid has been determined. The structure is built up of S—P pairs. Its unit cell is very like those of the components, but the symmetry is lower: $P\ 2_1$ instead of $P\ 2_1/a$. To get disordered 1:1 phases, which are of technical importance, the number of solid $\rightleftharpoons$ liquid transitions should be limited, the lowest possible temperatures should be used and solidification accomplished as rapidly as possible.

Long chain alifatic materials of biological and technical importance are generally complicated mixtures of several related compounds, *e.g.* homologous members of series such as fatty acids, glycerides and sodium soaps. Although the number of components is very often larger than two, binary systems are the only ones which have been fairly well investigated.

PHASE DIAGRAMS

Smith [1] summarizes the phase diagrams of binary systems of homologues of long chain alifatic compounds, classifying them into three different types: continuous series of solid solutions (with no maximum or minimum or with minimum), eutectic mixtures, and compound formation (with congruently or incongruently melting compounds). To the last category belong the binary systems of homologues of normal chain acids, methylesters, iodides, amides, anilides [1] and triglycerides [2]. The pure components of these systems all form double molecular sheets in the solid state. Compound formation has also been observed under certain conditions between normal fatty acids and *anteiso*- and *iso*-acids[3,4] and between normal amides and *anteiso*-amides [3]. Varying the polar groups or the position of the polar group often seems to give simple eutectic mixtures [1], *e.g.* 11-bromohendecanoic acid and 10-bromohendecanoic acid [5]. This is not unexpected, of course, considering steric variations as well as the variation in chemical bonding between the different polar groups.

Of the binary systems between homologues showing compound formation, the stearic acid — palmitic acid system (here called the S—P system) has been the most extensively investigated. In 1898 de Visser [6] published the first phase diagram of the S—P system using very pure components (setting point 69.32°C and 62.62°C, respectively). It indicates an incongruently melting compound at 50 % (s.p. 56.4°C) with an eutectic point at 54.8°C and 27.5 % S. This phase diagram has later been confirmed by Francis *et al.*[7], Schuette and Vogel [8] and Rawitsch and Volnova [2]. The last two investigators succeeded also in getting an eutectic point (55.9°C, 59 % S) on the S side of the compound by extremely slow cooling of the melts, thus having better equilibrium conditions. Similar phase diagrams for systems of other even-numbered fatty acids have also been found [8–13]. There seems to be no ambiguities or uncertainties about the phase diagram and its interpretation for the S—P system, and we have accepted it as correct.

The fact that there is a 1:1 compound formed in the solid state between stearic and palmitic acid has been said by some authors to imply necessarily the existence of S—P pairs instead of S—S pairs and P—P pairs in the compound structure. This is, however, not theoretically necessary, as the lattice in principle can be equally well built up with, *e.g.*, one S—S pair and one P—P pair in each unit cell instead of two S—P pairs.

Sarkadi and de Boer [14] find from infrared absorption measurements that the association degree for fatty acids in the liquid state, *e.g.* 0.953 at 123°C for stearic acid, is almost independent of chain length. If this is assumed to be exactly true, there will be equally many S—P pairs in the 1:1 melt as there are S—S and P—P pairs together, so whatever pairs the crystal structure contains, considerable time is required at the solidification point for the completion of the reaction 2 S—P $\rightleftharpoons$ S—S + P—P. As has been pointed out already, the best phase diagrams are obtained by extremely slow cooling [2,9].

LONG SPACING INVESTIGATIONS

The long spacing, which is frequently given for long chain compounds, is the perpendicular distance between planes containing the end groups of the molecules. Such measurements with X-rays on the S—P system have been performed by Slagle and Ott [15], Francis *et al.*[7] and by the authors. The result for specimens crystallized from melt is summarized in Fig. 1, where our own values are included. The pure acids give only one long spacing value (the C-form) when crystallized form melt. On rapid cooling of specimens of intermediate compositions, only one long spacing value is found as well [7,15] (Fig. 1), but on slower cooling two spacings may appear at compositions separated from 0, 50, and 100 %. The values group themselves around three spacings: 39.9 Å (the C-form of S), 36 Å (35.5 Å for the C-form of P) and 38.6 Å suggested by Francis *et al.*[7] to be the long spacing of the 1:1 compound.

Francis *et al.*[7] have also investigated S—P specimens crystallized from solvent, but the result of that investigation falls outside the scope of this paper.

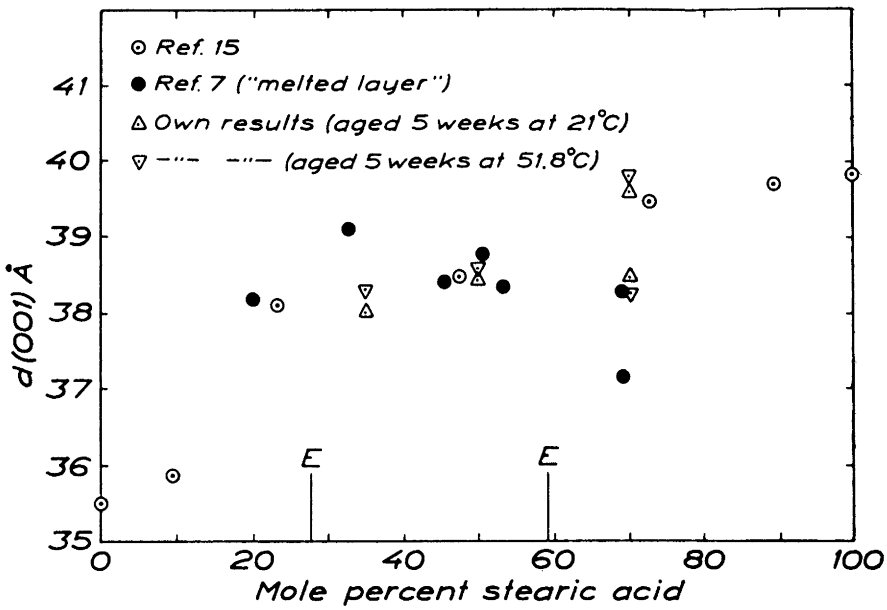

Fig. 1. Long-spacing as a function of composition for S—P specimens crystallized from melt. E = Eutectic composition.

In this work we are mostly dealing with the 1:1 compound, which has been investigated with X-ray powder and single crystal methods. The result is correlated with the structural behaviour of the components, which has been described by von Sydow [16] and Abrahamsson and von Sydow [17] and with the known crystal structures of homologues of the components: lauric acid determined by Vand *et al.*[18] and *n*-hendecanoic acid determined by von Sydow [19]. These structures have the orthorhombic chainpacking with every second chain plane perpendicular to the others [16]. The structures can be classified as O⊥ (021), if *a* is the shortest axis, following a suggestion by Vand [20] complemented by von Sydow [21].

MATERIAL USED

The very pure acids used were kindly put at our disposal by Prof. E. Stenhagen. The stearic acid has m. p. 69.4—69.7°C, and the palmitic acid has m. p. 62.6—62.9°C, as compared with 69.6 and 62.9°C, respectively, given by Francis and Piper [22]. Mixtures of the acids with 35.1, 50.1 and 70.1 mole % stearic acid, respectively, were melted together in an oil bath and kept at 100°C for 15 min, in order to attain equilibrium. The temperature was then lowered below the solidification point at 0.75°C/min. Parts of the specimens were annealed at 51.8°C for 5 weeks.

X-Ray powder photographs were taken at 20°C in a Guinier camera using Cu $K\alpha$ radiation. KCl was mixed into the samples as a calibrating substance (a = 6.292 Å).

Single crystals from the 1:1 specimen of a fairly large size were investigated optically and in a Weissenberg camera. Two out of ten gave good diffraction pictures; they were mounted along the *a*- and *b*-axes, respectively. Rotation and Weissenberg photographs were taken, using very long exposure times.

THE 1:1 COMPOUND

The X-ray powder photographs of the 1:1 specimens compared with those of the pure components (C-form) immediately revealed a striking resemblance between the structure of the compound and components. The powder photograph of the compound was indexed with use of the single crystal data obtained and the cell dimensions were accurately determined. They are given in Table 1 together with the cell dimensions for the components *, taken from the work by Abrahamsson and von Sydow [17]. A suggestion by Kofler [23] that the 1:1 specimen is a "stabilisierte Zwischenphase" is thus not adequate. The short spacings given by Fieldes and Hartman [24] for two reflexions, which can be identified as (110) and (200), are roughly in agreement with our cell dimensions.

Table 1. Cell dimensions and calculated densities at +20°C and space groups for stearic acid (C-form), palmitic acid (C-form) and the 1:1 compound between the two.

	a Å	b Å	c Å	β	Long spacing $d(001)$ Å	Calculated density gcm^{-3}	Space group
Stearic acid C-form	9.357 ±0.020	4.956 ±0.004	50.76 ±0.08	128° 14′ ±6′	39.87 ±0.04	1.022 ±0.002	$P\ 2_1/a$
1:1 Compound of stearic and palmitic acid	9.46 ±0.04	4.96 ±0.01	49.13 ±0.20	128° 14′ ±8′	38.59 ±0.08	0.992 ±0.005	$P\ 2_1$
Palmitic acid C-form	9.42 ±0.02	4.96 ±0.01	45.73 ±0.08	128° 40′ ±6′	35.72 ±0.04	1.020 ±0.002	$P\ 2_1/a$

The fact that the unit cell of the 1:1 compound is approximately an "average" between the cells of the components, leads to a rather limited number of possible molecular arrangements. They are shown in Fig. 2 as deduced from the works by Vand *et al.*[18] and von Sydow [19]. The first one ($P\ 2_1/a$), which is also representative of either of the components, represents a completely disordered phase with 1:1 composition containing S—P pairs or S—S and P—P pairs or all three. This is, however, not a very probable solution for a phase diagram showing compound formation, but rather for a system with a continuous series of solid solutions, *e.g.* for hydrocarbons or ethyl esters [1].

The following arrangements in Fig. 2 are ordered phases. The two middle ones are built up with S—P pairs and have the space groups $P\ 2_1$ and Pa, which also are monoclinic but with a lower symmetry than $P\ 2_1/a$. The last one is built up with S—S and P—P pairs and has the triclinic symmetry $P\ \bar{1}$ with a *pseudo*-monoclinic unit cell. As can be seen from Fig. 2 it is a rather

* There seems to be a slight increase in the differences for the c-dimension and the long spacing with increasing chain length. Thus the error limits given for the coefficients P and p in the linear equations for c and d (001) should be doubled.

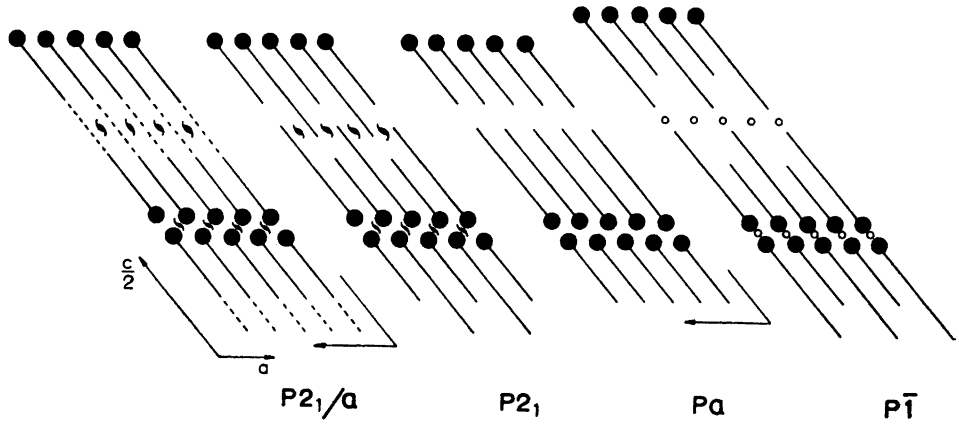

Fig. 2. Hypothetical molecular arrangements for the 1:1 compound between stearic and palmitic acid. $P\ 2_1$ is the correct one.

bulky structure with large holes in it and thus very improbable. A more close-packed arrangement of S—S and P—P pairs than the one to the right in Fig. 2 ($P\ \bar{1}$) will lead to a higher long spacing value (approximately twice the ones for the structures shown to the left in Fig. 2), which in one case (alternating S—S and P—P sheets through the crystal) should be easily measurable. In four cases (A- or B-centering of the $P\ \bar{1}$-type in Fig. 2) there will be systematic absences among the $00l$-reflexions for l odd, so the large real long spacing value will be halved. These four cases, which will be found inconsistent with the result from the single crystal measurements (see below), can, however, be ruled out at once from structural reasons, in that they will lead to the result that the chain planes of either two hydrogen bonded molecules or two molecules with close-packed end groups (CH_3-) are perpendicular. This has never been found to be the case for any crystal form of the normal fatty acids [16].

Each of the space groups of the four possibilities in Fig. 2 has different conditions for systematic absences, which are given in Table 2. Any possible deviation from $P\ 2_1/a$ will, however, be very weak, as all cases are *pseudo*-$P\ 2_1/a$, and the contribution will be from only two extra methylene groups on every second molecule. In order to secure the correct choice, very long

Table 2. Space group and absent reflexions for the four hypothetical molecular arrangements of the 1:1 compound (Fig. 2).

Space group	Conditions for systematic absences
$P\ 2_1/a$	$h0l$, when h odd and $0k0$ when k odd
$P\ 2_1$	$0k0$, when k odd
$P\ a$	$h0l$, when h odd
$P\ \bar{1}$	no

exposure times were used for the Weissenberg photographs. There was absolutely no trace of any $0k0$-reflextions with k odd, but $h0l$-reflexions with h odd appeared (Table 3). This definitely confirms the space group $P2_1$ and the molecular arrangement (marked $P\ 2_1$ in Fig. 2) for the 1:1 compound between stearic and palmitic acid. (The space group $P\ 2_1/m$, which has the same extinction conditions as $P\ 2_1$ has a mirror plane (m), which is inconsistent with the chain-packing [16].)

A comparison between the structure of the compound and the components (Table 1 and Fig. 2) reveals that the acid molecules are packed side by side in a slightly different way. This is caused by the puckered end group planes (Fig. 2), which when they are packed together, arrange themselves so they fit into the chain packing of the opposite sheet. This makes the c-dimension and long spacing higher than the arithmetic mean between those of the components. This is probably somewhat compensated by increased possibilities in van der Waals interaction over the methyl group gap [16] (Fig. 2). The result is, however, a less effective molecular packing for the compound than for the pure components, as revealed by the density 0.992 gcm^{-3} for the compound compared with 1.022 and 1.020 gcm^{-3}, respectively, for the components (Table 1). This is also consistent with the melting temperatures for the compound and the components given above.

It is now easy to understand the conditions for the formation of ordered and disordered phases of the 1:1 compound. If the melt contains few S—P-pairs, *i.e.* many S—S and P—P pairs, (by rapid melting together of the pure components at lowest possible temperature) and one wants an ordered phase, an extremely low rate of cooling must be used in the solidification, so that the reaction S—S + P—P → 2 S—P will take place completely. A repeated procedure of melting and solidification of the compound within a very small temperature interval should give the best ordered compound phase.

In technical processes of this kind there is generally a desire for obtaining disordered phases, however, as they are smoother and less grainy. To get such phases one should therefore limit the number of solid ⇌ liquid transitions, work at lowest possible temperatures and solidify as rapidly as possible.

Table 3. Observed reflexions $h0l$, which definitely establish the correct space group $P\ 2_1$ and the molecular arrangement for the 1:1 compound (Fig. 2). Visibility limit = 0.

I	hkl	I	hkl	I	hkl	I	hkl
0	$10\bar{9}$	0	$3,0,\bar{3}\bar{7}$	1	$30\bar{1}$	0	308
	*	0	$3,0,\bar{3}0$	1	300	0	3,0,23
0	101	0	$3,0,\bar{2}7$?	1	301		
		½	$30\bar{3}$	½	302	½	$5,0,\bar{2}\bar{3}$

* $10\bar{6}-100$ obscured by the beam stop.

TWO-PHASE MIXTURES

Several specimens from melt with compositions differing from 0, 50 and 100 mole % S were investigated with X-rays by Slagle and Ott [15] and Francis *et al.*[7] (Fig. 1). Their long-spacing values found are in excellent agreement with the phase diagram (except 37.1 Å for a composition of 69 % S[7]) considering the rapid cooling used.

These values have been complemented by investigating unannealed and annealed specimens with 35.1 % and 70.1 % S prepared under slow cooling. The first ones, which are between the P-eutectic point and the compound, show one diffuse long-spacing (Fig. 1) slightly lower than that for the 1:1 compound. The last ones, which are between the S-eutectic point and pure stearic acid, show two spacings (Fig. 1) corresponding to those of pure stearic acid and compound. This is in line with an observation by Francis *et al.*[7], that the palmitic rich phases have a more variable long-spacing than the ones rich in stearic acid. This is reasonable, as it must be easier to replace S-molecules with P-molecules in pure stearic acid than to replace P-molecules with S-molecules in pure palmitic acid. This is, of course, also the reason for the unsymmetrical phase diagram for the S—P system and for the difficulties in obtaining the S-eutectic point in comparison with the P-eutectic point, as it must be easier to make the compound richer in P than in S (Fig. 2).

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