

Crystallization of Normal Fatty Acids

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Normal fatty acids with 13, 15, 17 and 12, 14, 16, 18, 20, 22, 24, and 26 carbon atoms have been crystallized from pentane, ethyl ether, ethyl alcohol, acetone, ethyl acetate, benzene, carbon disulfide, carbon tetrachloride, and chloroform. The solid phases obtained have been investigated from the polymorphic point of view using a X-ray powder method.

Normal fatty acids exhibit polymorphism. The structures of the different polymorphic forms have been described by Vand, Morley and Lomer¹ (the C-form of lauric acid) and the author²⁻⁷ (the A'- and B'-forms of *n*-pentadecanoic acid, the B-form of stearic acid and the C'-form of *n*-hendecanoic acid). At present the A-form of lauric acid is being investigated. The D'-form of acids with an odd number of carbon atoms, said to exist by some authors^{8,9}, has never been found in investigations carried out here in Uppsala. Information about it is very scanty^{8,9}.

By varying the mode of crystallization and the temperature, the different polymorphic forms can be obtained either singly or two together. This behaviour has been studied many times using X-ray methods, the most recent being by E. Stenhagen and the author¹⁰. (For earlier results see Ref.¹⁰).

In this investigation normal fatty acids with 13, 15, 17 and 12, 14, 16, 18, 20, 22, 24 and 26 carbon atoms have been crystallized from the following solvents: pentane, ethyl ether, ethyl alcohol, acetone, ethyl acetate, benzene, carbon disulfide, carbon tetrachloride, and chloroform.

MATERIAL USED

The acids used are the same as those used by Stenhagen and the author¹⁰ and their preparation is described in Refs.¹⁰⁻¹². The melting points of the acids given in these papers agree very well with those given by Francis and Piper¹³.

EXPERIMENTAL

The crystallizations from the different solvents were carried out at +19°C and -14°C in order to study the influence of the rate of crystallization on the result.

Table I.

Number of carbon atoms in the fatty acid	Temperature °C	Solvent									
		$n\text{-C}_8\text{H}_{17}$	$(\text{C}_4\text{H}_9)_2\text{O}$	$\text{C}_2\text{H}_5\text{OH}$	$(\text{CH}_3)_2\text{CO}$	$\text{CH}_3\text{COOC}_2\text{H}_5$	C_6H_6	CS_2	CCl_4	CHCl_3	
13	+19°	A'	A'	A'	A'	A'	A'	A'	A'	A'	
	-14°	A'	A'	A'	A'	A'	—	A'	A'	A'	
15	+19°	A'	A'	A'	A' > B'	A'	A'	A'	A'	A'	
	-14°	A'	A'	A'	A'	A'	—	A'	A'	A'	
17	+19°	B'	B'	B'	B'	B'	B'	B'	B'	B'	
	-14°	B'	B' > A', A' > B', A'	B'	B'	B' > A'	—	A' > B'	B' > A'	B' > A', A'	

> more of the first phase or equal.

Table 2.

Number of carbon atoms in the fatty acid	Temperature °C	Solvent									
		$n\text{-C}_6\text{H}_{13}$	$(\text{C}_4\text{H}_9)_2\text{O}$	$\text{C}_2\text{H}_5\text{OH}$	$(\text{CH}_3)_2\text{CO}$	$\text{CH}_3\text{COOC}_2\text{H}_5$	C_4H_6	CS_2	OCl_4	CHCl_3	
12	+19°	C	C	C	C	C	C >> A	A	C >> A	A > C	
	-14°	A	A >> C	A > C, A	A	A > C	—	A	C > A, A >> C	A > C	
14	+19°	C, A	C, A > C	C	A > C	C	C	A	C	C > A	
	-14°	A	A > C, C > A	C, A >> C	A >> C	A	—	A > C	A	A	
16	+19°	C	C > A, A	C > A	C > A	C, A > C	C >> A	C > A	C >> A	C >> A	
	-14°	A > C	B	B	B	B	—	A > B	C	A	
18	+19°	C > A	C, C > B	C	C	C > B	C > B	C >> B	A > C	C > B, B > C, B	
	-14°	A > C	C > B	B	C	B	—	A > C	A > C	C > B	
20	+19°	C	C >> B, B	B > C	C, C > B	C > B	C > B	C > B	C >> B, C > B	B > C	
	-14°	C	B > C	C > B	C	C > B	—	A > C	A > C	C > B	
22	+19°	C	C	C	C	C	C	C	C > B	C > B	
	-14°	C	C > B	C	C	C	—	C >> B	C	C	
24	+19°	C	C	C	C	C	C	C	C	C	
	-14°	C	C	C	C	C	—	C	C	C	
26	+19°	C	C	C	C	C	C	C	C	C	
	-14°	C	C	C	C	C	—	C	C	C	

> more of the first phase or equal, >> much more of the first phase

In some cases samples were taken from two or three different parts of the crystallization vessel. The specimens were cut with a razor to a fine powder, which was cautiously pressed on Scotch tape fixed on the sample holder.

Powder photographs were taken in a Guinier camera using $\text{CuK}\alpha$ radiation.

The phase analysis was carried out partly by measuring the long spacing¹⁰, $d(001)$, partly by comparing the photographs with those obtained in connection with the crystal structure investigations²⁻⁷.

RESULTS

The results are collected in Tables 1 and 2. The notations in each square belong to the same crystallization, but in some cases the crystalline solid has been divided into two or three parts before the phase analysis. In such cases the notations are given in order of decreasing rate of crystallization. *E. g.*, $C > B$, $B > C$, B means that the solid which crystallized first (on the walls of the crystallization vessel) consisted of more C - than B -phase. The next sample taken from the raised center of the bottom of the vessel consisted of more B - than C -phase, and in the periphery of the bottom, where the rate of crystallization was slowest, pure B -form was obtained.

The results will be discussed in a subsequent paper.

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