ACTA CHEMICA SCANDINAVICA 16 (1962) 755–759

Some Features of the Ternary System: Myristic Acid, Palmitic Acid and Isopalmitic Acid

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The melting point diagram of the ternary system, myristic acid, palmitic acid and isopalmitic acid has been recorded. A phase analysis of the isothermal section at 25°C by X-ray methods shows the existence of a ternary phase. Its composition is 50 % myristic acid, 15 % palmitic acid and 35 % isopalmitic acid. Structural data are given for the six phases found.

Many solidification point diagrams for ternary systems containing long-chain fatty acids have been recorded. Most of them are discussed by Baily [1]. No X-ray data seem to have been reported for such systems of acids.

This investigation is part of a program of studying multicomponent systems of long-chain compounds. Earlier work has concerned binary systems of normal and branched-chain fatty acids [2–4].

EXPERIMENTAL

The melting points of the different samples representing about one hundred points in the ternary system were obtained in a Kofler heating stage microscope. The acids were fused together and shockfreezed. The samples were then carefully melted, partly resolidified and the temperature recorded when the last crystals again disappeared on heating.

X-Ray Guinier powder photographs of the samples at 25°C were taken with Cu$K\alpha$ and Cr$K\alpha$ radiation. Samples for the X-ray work were obtained by slow crystallization from the melt. The samples were brought to a temperature well above their melting points and the temperature then lowered to room temperature in a thermostat over a period of several days.

The acids were kindly provided by Prof. E. Stenhagen. The melting points of the acids are: myristic acid [5] 54.4°C, palmitic acid [5] 62.9°C and isopalmitic acid [6] 61.6°C.

In the following discussion myristic acid will be called n-C_{14}, isopalmitic acid 14Me-C_{15} *etc.*

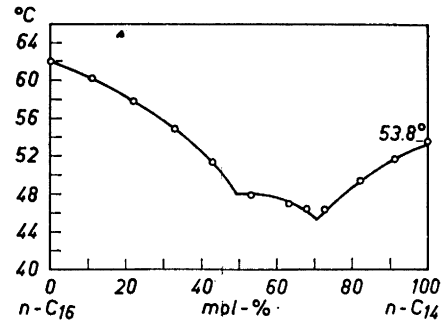

Fig. 1. Melting point diagram of the binary system n-C_{14}—n-C_{16}.

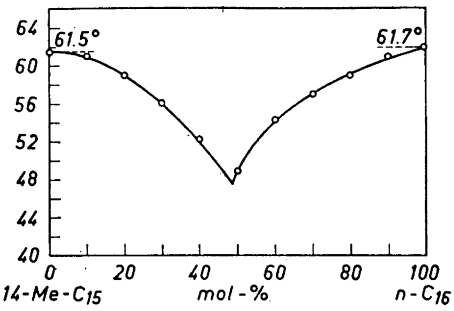

Fig. 2. Melting point diagram of the binary system 14Me-C_{15}—n-C_{16}.

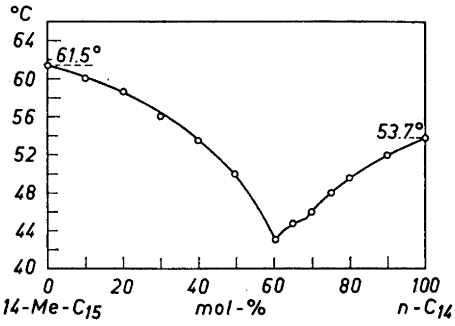

Fig. 3. Melting point diagram of the binary system 14Me-C_{15}—n-C_{14}.

RESULTS AND DISCUSSION

The melting point diagrams of the binary systems of the components are shown in Figs. 1—3. The systems of the normal acids contain a (1:1) molecular compound. The system 14Me-C_{15}—n-C_{16} is of the simple eutectic type whereas the diagram of the system 14Me-C_{15}—n-C_{14} indicates the presence of a (1:3) compound. This is all in accordance with the results of Abrahamsson and von Sydow [4].

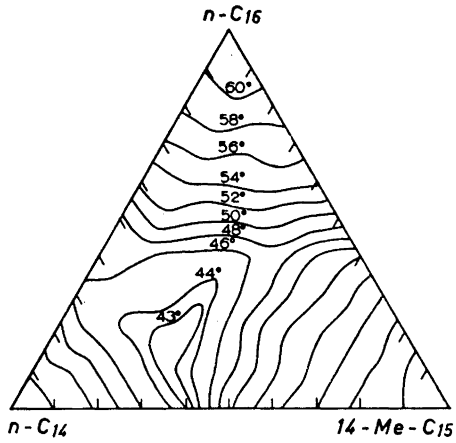

Fig. 4. Melting point isotherms in the ternary system n-C_{14}—n-C_{16}—14Me-C_{15}.

Melting point isotherms in the complete ternary system are given in Fig. 4. A space model was constructed on the recorded melting points but it gave only a crude outline of the melting point surfaces. The lowest melting point is at 42.4°C at a composition of about 60 % n-C_{14}, 10 % n-C_{16} and 30 % 14Me-C_{15}. The ternary system of the normal acids n-C_{14}, n-C_{16} and n-C_{18} is similar in having its lowest melting point at 42.3°C at about 67 % n-C_{14}, 12 % n-C_{16} and 21 % n-C_{18} [1].

The powder photographs of the different samples at 25°C were studied and the phases existing in different regions of the ternary system were determined. The isothermal section is outlined in Fig. 5. It was not possible to find the

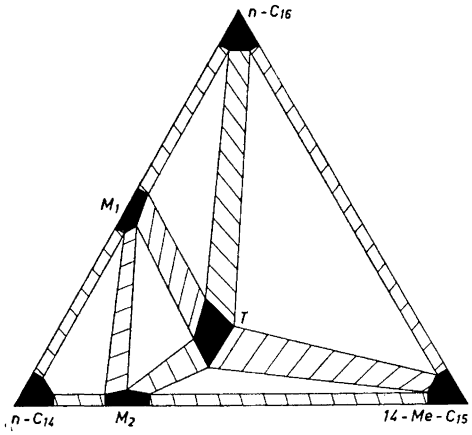

Fig. 5. Isothermal section (25°C) of the ternary system n-C_{14}—n-C_{16}—14M-C_{15}. Black regions represent single phase areas and shaded regions two phase areas.

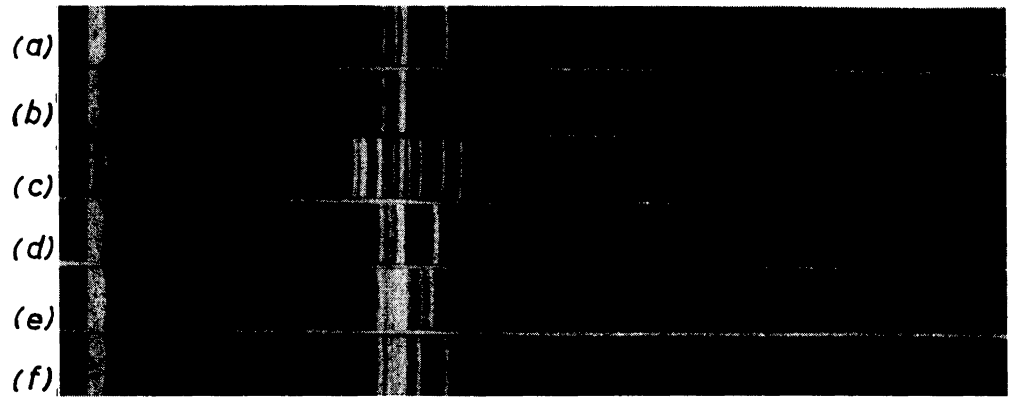

Fig. 6. Powder photographs of the different phases in the ternary system: a) n-C_{14}, b) n-C_{16}, c) 14Me-C_{15}, d) molecular compound M_1, e) molecular compound M_2 and f) ternary compound T. The powder photographs of M_1 and T indicate that they are based on mainly single phase samples whereas that of M_2 shows lines of n-C_{14} as well because M_2 melts incongruently.

actual limits of the different areas and the phase regions drawn are intended to be illustrative only.

As seen from Fig. 5 there exists a ternary compound (T) in the system. It has a composition of 50 % n-C_{14}, 15 % n-C_{16} and 35 % 14 Me-C_{15}. In all, six phases are found in the ternary system and the outlined subdivision seems the only one compatible with the phase analysis.

Phases present. (1) n-C_{14} and (2) n-C_{16}. The normal fatty acids in the system have the C-form structure with the carbon chains in the common orthorhombic chain packing (O$\perp$). Every second chain plane is thus roughly perpendicular to the others. The molecules are held together to dimers by hydrogen bonds and are tilted about 56° towards the end group contact planes (*cf.* von Sydow [7]).

(3) 14Me-C_{15}. The molecules of isoacids are forced to be much more tilted than those of normal acids to allow accomodation for the methyl branches between the tails of the dimer molecules [8]. The angle between the chain axes and the end group planes is thus only about 45°. The chain packing is triclinic with all chain planes parallel (T$\parallel$).

(4) Molecular compound M_1. The compound is analogous to the binary phase in the system stearic acid-palmitic acid. The latter has been shown by Degerman and von Sydow [3] to contain dimers of one molecule stearic acid and one molecule palmitic acid packed essentially the same as the dimers in the C form of normal fatty acids. The long spacing of the molecular compound is accordingly intermediate to those of the components as is also shown in this case where M_1 has $d(001)$ = 33.7 Å whereas n-C_{16} and n-C_{14} have $d(001)$ = 35.7 Å and 31.6 Å, respectively (Table 1). The similarity of the powder photographs of M_1 and the components is obvious from Fig. 6.

Table 1. Long-spacings of the different phases in the ternary system.

Phase	d(001) Å
n-C_{14}(C-form)	31.6
n-C_{16}(C-form)	35.7
14Me-C_{15}	30.2
Molecular compound M_1	33.7
» » M_2	32.2
Ternary compound T	33.7

(5) Molecular compound M_2. In a system corresponding to that of 14Me-C_{15} and n-C_{14} but containing an isoacid with an odd number of carbon atoms (23Me-C_{24}—n-C_{23}) Abrahamsson and von Sydow [4] found that the (1:3) compound has a long spacing similar to that of the normal acid (n-C_{24}) derived from the unbranched part of the isoacid. The carbon chains of the compound follow the orthorhombic chain packing (O⊥). As can be judged from the powder photographs M_2 is similar in having the same chain packing but has a long spacing (32.2 Å) which is shorter than that of the most tilted polymorph of n-C_{15} [5] (34.5 Å). It is not surprising that structural differences should exist in these binary phases depending on whether the isoacid contains an odd or an even number of carbon atoms.

(6) Ternary compound T. The powder photograph of the ternary phase is given in Fig. 5 f. T has the same long spacing as M_1 (Table 1) but shows distinctly different side spacings. The powder diagram indicates that the carbon chains are arranged in the orthorhombic chain packing (O⊥) but it shows no other similarities to the powder patterns of known fatty acid structures.

It has not been possible so far to grow single crystals of M_2 and T and detailed structural information is thus lacking about these two phases.

Acknowledgement. We wish to thank Prof. G. Hägg and Prof. E. Stenhagen for their interest in this work and for laboratory facilities. We also thank Dr. S. Rundqvist for helpful discussions and Mrs. M. Innes and Mr. L. Ahlquist for technical assistance.

The investigation has been supported by grants from the *Swedish National Science Research Council* and (in part) by grant A-4006 from the *U.S. Public Health Service.*

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Received October 10, 1961.