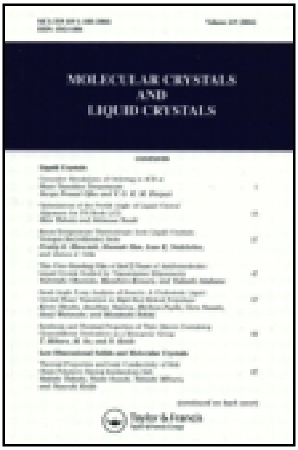

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ON THE INTERPRETATION OF THE HIGH RESOLUTION NMR SPECTRA OF SOLID FATTY ACIDS - THE ROLE OF IMPURITIES.*

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ABSTRACT ^{1}H NMR evidence is presented for stearic acid ($C_{17}H_{35}COOH$) doped with H_2O or stearyl alcohol which shows that the recently reported high resolution spectra of solid long-chain fatty acids may be interpreted solely in terms of the impurity content of the materials without recourse to "monomeric" postulates.

It has long been known[1] that long-chain fatty acids crystallize as linear hydrogen-bonded dimers arranged side by side and that the various structural modifications or phases arise in part from variation in the angle of tilt of the linear dimer axis (the c-axis) with respect to the plane of the hydrogen-bonded carboxyl groups (the a-b axes plane). Also it is well recognised, from the broad-line ^{1}H nmr studies of Dunell and co-workers in particular, that even well below the melting point, solid samples of long-chain fatty acids contain liquid-like regions which give rise to narrow nmr lines, the integrated intensity of which depends on temperature, thermal history and impurity content.[2-5]

Recently two reports have appeared dealing with anomalies in the properties of fatty acids at temperatures just below the melting point. The first,[6] describing an adiabatic calorimetric study of

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stearic acid, suggested the existence near the melting point of an unknown phase in addition to the usual stable C form. It was not resolved, however, whether the new phase arose from impurities or whether it was intrinsic to stearic acid itself. The second report[7] dealt with both ^1H and ^{13}C high resolution nmr spectroscopy of the solid phases of the series of long-chain fatty acids from C_{15} to C_{19} at various temperatures near the melting point. The ^1H spectra illustrated in that report show several narrow lines which increase in sharpness as the temperature approaches the melting point. In addition, two of the proton lines, one near $\delta = 4$ ppm and one near $\delta = 12$ ppm (the latter arising from the carboxylic proton), were found to concomitantly decrease and increase in amplitude, respectively, as the temperature increased. As a result of the apparent correspondence between these two lines it was surmised[7] that the 4 ppm line (not observed for the even acids nor for the liquid phase) arose from the carboxylic acid proton of monomeric acid molecules present in the solid crystalline lattice. It was also noted[7] that the narrow line observed at 12 ppm in the spectrum of the solid phase broadened and shifted up-field as its amplitude decreased.

Some peculiarities, however, are apparent in those data. Firstly, the inference that monomeric carboxylic acid molecules only occur in detectable quantities in the odd series of these acids is surprising although it must be acknowledged that on occasion significant differences are found between odd and even members of such homologous series. Secondly, the proton line near 4 ppm showed an increase in both amplitude and width as the temperature of the solid was decreased from the melting point. This implies an increase in the number of monomeric acid molecules with decreasing temperature which suggests the assignment of the 4 ppm line to monomer acid units to be incorrect, since, on a simple energetic basis alone, one would expect a decrease in the number of such species with decrease in temperature rather than the increase implied by the experimental observations. Furthermore, the relatively narrow nmr lines, of width less than 10 Hz, observed in the high resolution spectrum of the solid phase show that the acid molecules under observation here, possess freedom in both translational and reorientational senses and consequently must be associated with the liquid regions surrounding impurity centres and lattice defects described by Dunell and co-workers.[3-5] Thus the usual temperature dependent solubility effects must be operative. i.e. the number of acid molecules contained in these regions must decrease as the temperature is decreased.

Since the implications of the earlier work[2-5] appear to have been missed we have re-examined at high resolution the ^1H spectrum of one of the even acids studied by Kimtys[7] but using an exceptionally wide sweepwidth. We find the narrow lines to be superimposed upon a wide-line spectrum typical of a non-rotator phase solid and we show that the features of the spectra reported by Kimtys for the odd numbered acids may be easily reproduced in the even-numbered acids by the addition of an hydroxyl-containing impurity. Our results for stearic acid (C_{18}) may be entirely explained by reference to such an added impurity without the need to invoke such a concept as the occurrence of monomeric fatty acid molecules in the solid phase.

High resolution ^1H spectra were obtained at 180Mhz at several temperatures using a Bruker CXP-180 NMR spectrometer operating in the high-power mode without sample spinning. For each spectrum up to one hundred free-induction decay transients were co-added. Eastman-Kodak White Label grade stearic acid ($C_{17}H_{35}COOH$) was used without further purification, fresh samples of which showed virtually no signs of narrow absorption lines below 303K. The latter could be seen, however, with increasing ease as the temperature was raised to near the melting point. Doped samples of stearic acid were prepared by adding the impurity dopant to the solid followed by melting and subsequent recrystallization.

Figures 1a and 1b show ^1H spectra obtained at 332K and 313K for a water-doped stearic acid sample (2% by wt H_2O) under high resolution conditions with a relatively narrow sweep-width of 10Khz. With decreasing temperature both the decrease in intensity of the acid proton signal (seen here near 10 ppm)

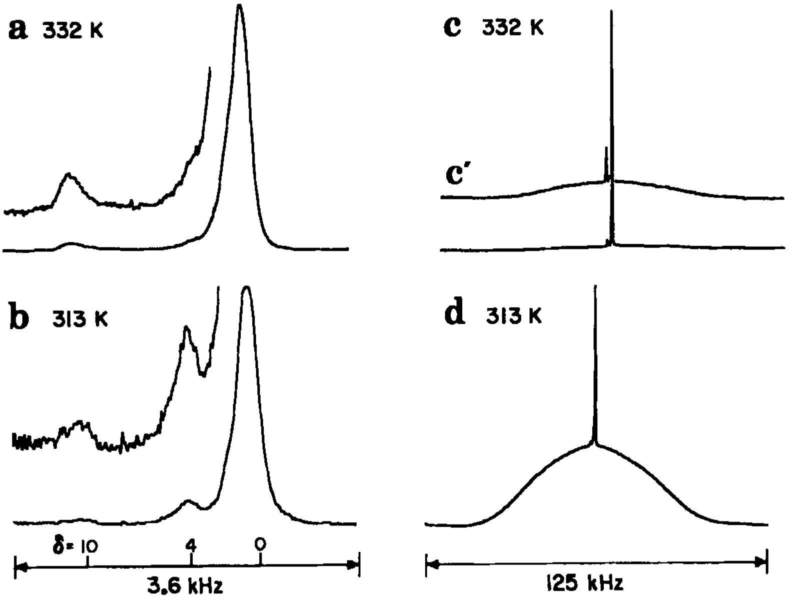

FIGURE 1. High resolution ^1H nmr spectra of stearic acid doped with 2% by wt H_2O obtained under conditions of narrow (a,b) and wide (c,d) sweep-width.

and the increase in intensity of the 4 ppm signal are, as reported by Kimtys for the odd-numbered species only, clearly in evidence.

Figures 1c and 1d illustrate spectra obtained for the same sample and at the same temperatures as before but using a much greater sweep-width (namely 125Khz). It is evident that the high resolution spectrum is superimposed on the much broader spectrum arising from the bulk solid phase. In the case of the spectrum obtained at 313K (fig 1d), the narrow line spectrum so characteristic of liquid is obviously representative of only a few percent of the protons in the sample. In contrast, at 332K (fig 1c), eleven degrees from the melting point, the contribution from liquid is much greater and the wide-line element of the spectrum, characteristic of solid, is all but indiscernible except on the expanded plot c′, although it still contributes significantly to the integrated intensity of the spectrum.

The narrow-line features of figure 1 can be explained in terms of the liquid-like regions associated with impurity centres and lattice defects as follows. In the melt, and just below the melting point, impurity protons form only a very small proportion of the protons contained in the liquid-like regions. Thus the signal seen near 4 ppm in figure 1a is very weak. With decreasing temperature an increasing amount of the carboxylic acid dissolved in the liquid-like regions crystallizes out (the inverse of premelting), the liquid-like regions become relatively richer in impurity, the impurity protons thus form an increasing proportion of the total proton population of the liquid-like regions and so the 4 ppm line becomes stronger (figure 1b). At the same time, the carboxylic proton signal seen near 10 ppm broadens and decreases in amplitude as the carboxylic acid content of the liquid-like regions decreases. The line broadening and up-field shift seen in the data of Kimtys are not so greatly in evidence, however, in our spectra.

Additionally, our experiments show both the carboxyl proton signal and the impurity proton signal to be equally sensitive to the nature and quantity of the added impurity. For instance, increasing the water content by a factor of two caused the acid proton signal to broaden significantly and to shift up-field, the impurity proton signal increasing in amplitude and shifting from 4.1 to 4.5 ppm. In another instance, the addition of 2% by weight of stearyl alcohol to a stearic acid sample caused the appearance of an impurity proton line at 5.3 ppm the intensity of which depended upon temperature in much the same way as was observed for the water-impurity signals. For this sample the carboxylic proton signal was temperature insensitive within experimental error over the temperature range studied.

We conclude from these considerations that the results of Kimtys[7], presented as being peculiar to the odd-numbered members of the fatty acid series, are typical of all systems of this type containing some small degree of impurity, the exact nature of which remains in doubt, although in the cases considered here an hydroxyl-containing species is undoubtably involved. It is well recognised that long-chain compounds are difficult to prepare in a pure state and in the cases of alcohols and acids in particular, which contain strongly hydrophilic groups, the elimination of moisture is exeedingly difficult. The apparent differences between the odd and even members found by Kimtys[7] must be ascribed to the well known fact that the even members of such homologous series are usually more readily obtainable in a purer state than are the odd members. Vacuum sublimation as employed by Kimtys cannot be considered an effective method of purification of these compounds.

The observation of high resolution spectra for such solid systems offers some promise as a method for studying, as in this instance, the role of impurities in the onset of phase transformations. The method should also have considerable applicability in the broader field of phase equilibria in general. It should be easy to apply the technique to the observation of eutectic liquid and hence to the determination of reasonably accurate composition data. Full regard should be given, however, to the misleading consequences of incomplete attainment of thermodynamic equilibrium.

Finally, concerning the recent report of Koga[6] mentioned earlier, in view of the foregoing discussion we would suggest that our observations perhaps favour an interpretation of the calorimetric data in terms of an impurity hypothesis.

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