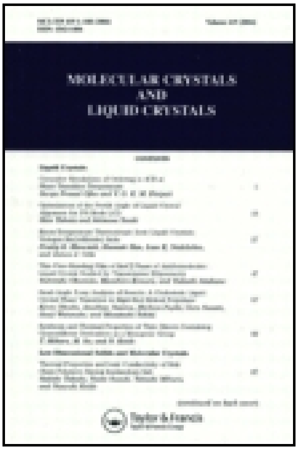

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ANOMALOUS DEFECT/IMPURITY DOMINATED DIELECTRIC BEHAVIOUR OF LAURIC ACID IN THE SOLID PHASE*

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ABSTRACT The dielectric permittivity and loss of solid lauric acid ($C_{11}H_{23}COOH$) at audio and radio frequencies are reported for the temperature range from 1.5K to near the melting point. No features attributable to configurational interchange within the acid-dimer groups are observed. The peculiarities of the data are discussed in terms of the liquid-like regions associated with impurity and defect centres.

The solid phases of the long-chain fatty acids have been extensively investigated.[1] X-ray evidence[1,2] has shown the acid molecules to be orientated within the crystal lattice as "head to head" dimers, the carboxyl "head" groups forming eight membered rings having essentially a centrosymmetric chair conformation; infra-red evidence[3,4] has pointed to configurational changes within the dimeric acid group as a function of temperature; and NMR evidence[5-7] has indicated that impurities and lattice defects play an important role in the various manifestations of molecular motion within these crystalline solids.

The infra-red evidence[3,4] has been interpreted in terms of the coexistence of two molecular configurations within the crystalline lattice, the cis form being the more stable for the C_4 and C_6 acids and for those of the odd series, and the trans form being the more stable for those acids of the even series from C_8 up, cis and trans refering to the relative configuration of the β-carbon and the carbonyl oxygen. Several isomerization mechanisms have been proposed[3,4] ranging from that of a simple overall concerted reorientation of the eight-membered dimer ring

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to that of an internal double proton transfer. It has been suggested[3] that the former mechanism would lead to "a sharp transition" presumeably below which the interchange rate would be expected to be exceedingly slow. However, since the infra-red spectra vary only gradually with temperature the latter mechanism has found favour. Processes involving twisting or distortive ring motions which would destroy the centrosymmetric character of the dimer ring appear to have been ruled out.[4] The presence of a centre of symmetry, of course, renders the configurational interchange involved, no matter what the mechanism, dielectrically inactive. Thus the dielectric constant or permittivity would be expected to be low and the dielectric loss ideally should be zero. Nevertheless, any "sharp transition" would be expected to manifest itself as a discontinuity either in the permittivity itself or in its rate of change with temperature. Also, the fatty acids show evidence of considerable liquid-like molecular motion in the solid phases at temperatures appreciably below the melting point,[5-7] thus a region of dielectric absorption associated with such motion is anticipated. Since only the microwave dielectric properties of the long-chain fatty acids are known,[8] the audio and radio frequency dielectric properties appearing not to have been reported, it was presumed to be worthwhile to examine at least one member of the series. Accordingly, the low frequency dielectric permittivity E′ and dielectric loss E″ of lauric acid are reported here for the temperature range from 1.5K to near the melting point.

EXPERIMENT

A sample of the C-form of lauric acid ($C_{11}H_{23}COOH$), prepared from the melt and stored over P_2O_5, was kindly supplied by J. Umemura. The sample, examined by differential scanning calorimetry, showed no sign of the presence of any other structural modification and melted at 44.0°C, slightly lower than the highest reported values (44.5-8,[9] 44.8[1]). Two disc-shaped dielectric specimens were prepared by pressing the powdered material in a 3/4" diameter die. The first, of thickness 0.102", was of density 1.01±0.01gm/cc, and the second, 0.036" and 1.05±0.03gm/cc, repectively (lit: ρ=1.032gm/cc)[1]. Permittivity E′ and loss E″ were measured, using a parallel-plate three-terminal cell and a General Radio 1615A bridge, over the ranges 500Hz to 60KHz in frequency and 1.5K to 330K in temperature. The electrical and cryostat systems were as described previously.[10] In order to minimise the effects of inter-electrode air gaps caused by inevitable surface irregularities the surfaces of the second sample were coated with petroleum jelly prior to insertion of the sample within the dielectric cell. No significant improvement in the measured permittivity which could be ascribed to this procedure was observed, however, although there was a marked absence of ionic conductivity effects for this sample. Also for this sample the measured permittivity was somewhat lower probably because the actual interelectrode spacing was slightly greater than the real sample thickness (from which the cell constant was calculated) because of the presence of the surface coating.

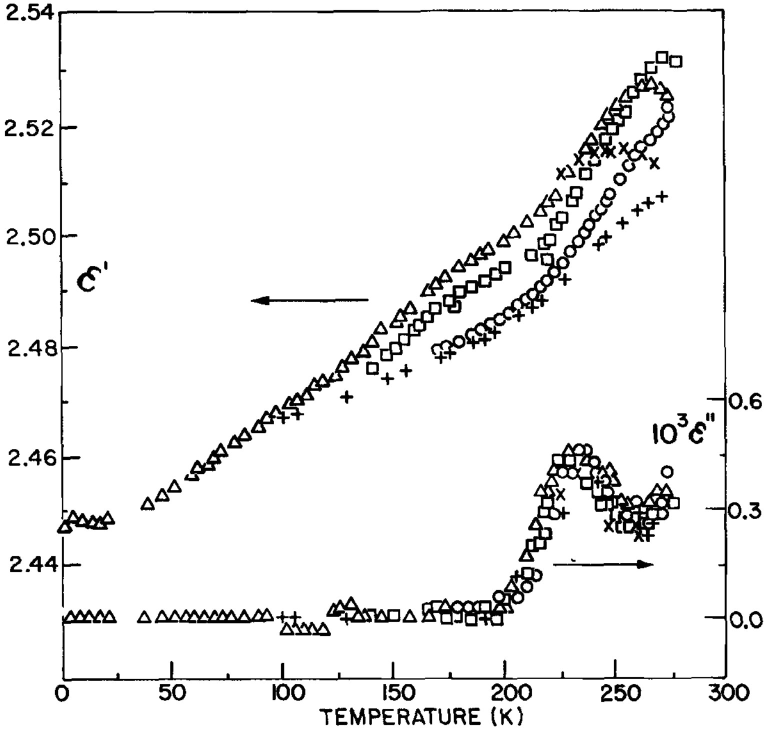

FIGURE 1. Permittivity E' and loss E" of lauric acid sample #1. □ cooling, ○ warming, △ cooling, + warming, × cooling.

RESULTS

The permittivity E' and loss E" measured at 10KHz for sample 1 are shown in Fig 1. The characteristic features are a pronounced variability in the permittivity values between subsequent cooling and warming runs and a very small, somewhat less variable, apparent loss peak of amplitude E"=0.0005 occuring at temperatures near 230K. The situation is qualitativly similar for sample 2 (Fig 2), here, however, the incipient permittivity maximum seen near 180K in Fig 1 is more clearly resolved and the apparent loss peak, now centred near 250K, is larger by a factor approaching two. The ionic conduction current, evidenced for sample 1 by the upswing in E" in Fig 1 at temperatures above 255K, appears to have been effectivly blocked in the case of sample 2 by its surface treatment. In Fig 1, the small increase in permittivity near 5K is a nugatory experimental artifact occasioned by temporary contamination of the sample and electrode region by the liquid helium cryogen. In the range 1.5K to 200K the dielectric loss is essentially zero. The values of permittivity reported here for lauric acid are quite consistent with (although perhaps slightly higher than) the microwave values reported by Buchanan.[8]

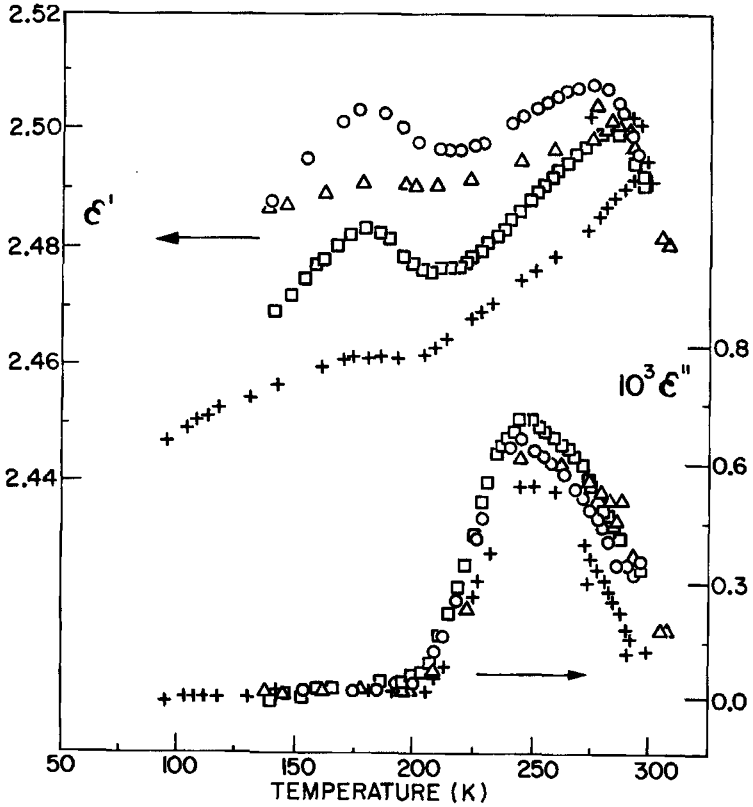

FIGURE 2. Permittivity E′ and loss E" of lauric acid sample #2. □ cooling, ○ cooling, △ warming, + warming.

DISCUSSION

Firstly, the dielectric results show no features which can be ascribed to the cis-trans configurational interchange process dicussed in the introduction. The overall results are entirly consistent with the accepted centrosymmetric acid dimer structure and as such throw no light on the nature of the interchange mechanism involved in the isomerization except insofar as the absence of any significant discontinuities in E' and $\delta E'/\delta T$ with temperature favours the proton transfer hypothesis.

The feature of the results of greatest significance is the irreproducibility of the data after thermal excursion. This implies a persistence of thermodynamic dis-equilibrium in the solid which persists even after extensive thermal equilibration. That this must be associated with impurity centres and lattice defects there is little doubt. The NMR evidence has been shown clearly[5-7] to demonstrate that regions exist in the crystalline lattice where the regular lattice order is disrupted and where acid molecules themselves as well as impurity molecules are able to undergo motions akin to those occurring in the liquid state. Accordingly, the variability of the measured permittivity must arise from variation in the size and polarization of these liquid-like regions and from failure of these regions to follow conditions of thermodynamic equilibrium within the timescale of the experiment. That the variability does not arise either from thermal hysteresis or from mechanical instability within the dielectric cell is proved by the absence of suitable correlation between the variability of the permittivity data and that of the loss data. The specific features of the results may be explained as follows.

The permittivity of most dielectric materials increases with increasing density, that is to say, decreases with increasing temperature. For certain solids the inverse is true as is the case here. This inverse situation arises from the temperature dependence of the low-lying translational lattice vibrations which absorb at lower frequencies at higher temperatures and so make a larger and larger contribution to the refractive index (and hence to the permittivity) as the temperature rises. This situation is commonly observed for ionic lattices such as NaCl[11] and for strongly hydrogen-bonded lattices such as that of hexagonal ice.[10] For the fatty acids the phenomena must be associated with the hydrogen-bonded acid groups.

The irregularities which occur above 180K must be ascribed to overall changes in density and polarization caused by the growth and shrinkage of the liquid-like regions as the temperature is varied. After repeated thermal excursion the irregularities become much less pronounced presumably as a result of annealing. Above 270K premelting effects become predominant and E' falls as the true melting point is approached.

In terms of dielectric loss both samples showed qualitatively the same behaviour (Figs. 1 and 2). Thermal cycling (annealing) caused the apparent loss maximum to decrease slightly which suggests that the loss features also are associated with the presence of the liquid-like regions. The greater amplitude of the apparent loss peak for sample 2 implies a higher concentration of defect/impurities in that sample as is implied also by the greater variability of its permitivity. Efforts to define these apparent loss peaks in terms of frequency at constant temperature showed them to be spurious in the sense that the experimentally observed loss maxima seen in the temperature domain at constant frequency do not in fact represent the true loss maximum of any relaxation process. Spectra taken between 500Hz and 60KHz at constant temperature between 218K and 295K showed increasing loss with increasing frequency implying the true relaxational loss maximum to lie at higher frequencies still. The observed loss maxima of Figs. 1 and 2 are explainable in terms of E" initially increasing with decreasing temperature as a result of the usual Arrhenius behaviour, then as the liquid-like regions gradually "freeze up" as the temperature is lowered further, fewer and fewer dipoles contribute to the relaxation process, so the real E"max amplitude falls and consequently so does the observed loss at the frequencies of measurement. The behaviour is typical of a system of relaxing dipoles with each dipole alternating between two positions of minimum but unequal potential energy. On cooling, the dipoles gradually become fixed in the orientation of minimum energy and consequently the relaxation strength as measured by E" falls.

It is unlikely that the observed dielectric loss is the tail-end of a higher frequency absorption associated with the cis-trans configurational interchange since if this were so then one would not anticipate any great irreproducibility in the measured data nor, and more importantly, any difference between different samples. Since for both samples E" was not reproducible and there was a factor of nearly two difference in E" between them we conclude the impurity/defect dominated explanation to be the most likely. This conclusion is further supported by a consideration of other hydrogen-bonded systems. Hexagonal ice provides a typical example with a dielectric relaxation time corresponding to frequencies of the order of 700Hz at 250K.[12] For ice, it is well known[12] that the presence of lattice defects and impurities leads to a considerable increase in the relaxation rate. In the liquid-like regions within the lauric acid crystal the hydrogen-bond picture can hardly be considered to be well defined, the presence of hydrogen-bonded hydrophillic species which undoubtably comprise the major portion of the non-paraffinic impurity within the system, must result in the acceleration of any hydrogen-bond relaxation process. Consequently the occurrence of absorption at higher frequencies is not surprising.

In conclusion it may be said that: no feature related to configurational change can be seen in the dielectric spectrum; the low frequency dielectric data for the solid phase of lauric acid is in accord with the centrosymmetric nature of the eight-membered dimer ring suggested by the structural data; and the peculiarities of the dielectric response may be interpreted in terms of the response of the liquid-like regions associated with impurity centres and lattice defects.

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