the bridge at temperatures above 107°. This indicated the presence of ionic impurities, probably traces of ammonium chloride retained from the synthesis despite repeated washings of a benzene solution of the amide with distilled water.

Cholesteryl Stearate.—The cholesteryl ester of stearic acid is of interest because it exhibits a liquid crystalline, or mesomorphic, state. Of the two types of liquid crystals, smectic and nematic, the cholesteryl esters above the myristate assume the smectic form.[16] Cholesteryl stearate was prepared by treating stearoyl chloride with cholesterol in pyridine solution. The ester was crystallized from ethanol. As is shown in Fig. 13, the liquid tended to supercool, and did not freeze until its temperature had dropped to 80°. Freezing was, therefore, accompanied by a slight spontaneous warming of the sample, and a drop in dielectric constant from 2.68 to 2.36. No further discontinuities appeared in the cooling curve. On warming, the break in the dielectric constant *vs.* temperature curve occurred at 81.5–81.6°. Ralston[17] lists the turbidity point (solid ⇄ liquid crystal) for cholesteryl stearate as 78°, and the melting point (liquid crystal ⇄ liquid) as 82.5°. The discontinuity at 81.5°, therefore, seems to correspond to the change from mesomorphic to liquid state. If this is so, then it appears that, in the mesomorphic state, the molecules are not free to orient themselves in an applied electric field, but rather are constrained as in the crystalline solid. There is, however, a possibility that the temperatures tabulated for the phase changes by Ralston are low, in which case the discontinuity observed at 81.5° may correspond to the change from the solid to the mesomorphic, or liquid crystal, state. In any event, one of the two phase changes involving the smectic state occurs without producing any discontinuity in the dielectric constant curve.

PRINCETON, NEW JERSEY

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(16) A. W. Ralston, "Fatty Acids and Their Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 565.

(17) A. W. Ralston, ref. 16, p. 566.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Hydrogen Bonding and Anomalous Dielectric Dispersion in Long-chain Alcohols and Mercaptans[1]

BY ARMAND DI GIACOMO[2,3] AND CHARLES P. SMYTH

RECEIVED OCTOBER 26, 1955

Solutions of tetradecyl alcohol and hexadecyl alcohol in molten dicetyl and in molten hexadecyl ether failed to form solid solutions on solidification. The resulting two-phase solid mixtures showed the same transition and melting points and the same dielectric behavior as the individual components. Tetradecyl mercaptan and octadecyl mercaptan are found to form a stable, non-rotator, solid phase and a metastable rotator phase with a region of anomalous dielectric dispersion at radio frequencies some distance below the melting point. As hydrogen bonding is very weak, if present at all in the mercaptans, the high dielectric constant and loss found for the rotator phase in the hydrogen-bonded long-chain alcohols is not observed.

The anomalous dielectric behavior observed for the rotator phases of long-chain alcohols[4-6] and 1-monoglycerides[7] has been attributed to a mechanism of proton transfer facilitated by rotation about their long axes of adjacent molecules capable of hydrogen bonding.[6-8] Although the effect is quite pronounced in the long-chain alcohols and monoglycerides, it was absent in the 1,3-diglycerides[9] which, although polymorphic, froze into an unstable non-rotator phase. Similarly, in long-chain amines,[10] only slight frequency dependence and loss were observed since the compounds studied appeared to freeze predominantly into the stable non-rotator form. The high d.c. conductivity which has been observed for polyamides may be due to movement of hydrogen ion resulting from isomerism in the amido linkage.[11] Cyclohexanol[12] and cyclopentanol[13] both possess a rotator phase. From their Cole and Cole arc plots, it was concluded that the entire molecule is free to orient in the lattice. Their dielectric constants and losses are perfectly normal. Proton transfer is, therefore, not possible, presumably because the hydroxyl groups are not located near to each other but are separated by distances of the order of the ring diameters. Triphenylcarbinol and cholesterol, which possess hydroxyl groups embedded in a bulky molecular structure, do not show the anomalous dielectric behavior.[14]

This paper describes experiments designed to examine further the role of protons in the anomalous dielectric behavior observed in those compounds.

Experimental Method and Results

Dielectric constants ϵ' were measured at frequencies of 0.5, 5 and 50 kilocycles by means of the impedance bridge and with the techniques previously described.[6,15] The experi-

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(1) This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) This paper represents a part of the work submitted by Mr. Armand Di Giacomo to the Graduate School of Princeton University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

(3) Procter and Gamble Fellow in Chemistry, 1951–1953.

(4) W. O. Baker and C. P. Smyth, THIS JOURNAL, **60**, 1229 (1938).

(5) K. Higasi and M. Kubo, *Sci. Papers Inst. Phys. Chem. Res.* (*Tokyo*), **36**, 286 (1939).

(6) J. D. Hoffman and C. P. Smyth, THIS JOURNAL, **71**, 431 (1949).

(7) R. W. Crowe and C. P. Smyth, *ibid.*, **72**, 4427 (1950).

(8) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, Chapter V, Sect. 4.

(9) R. W. Crowe and C. P. Smyth, THIS JOURNAL, **72**, 5281 (1950).

(10) J. D. Hoffman and C. P. Smyth, *ibid.*, **71**, 3591 (1949).

(11) W. O. Baker and W. A. Yager, *ibid.*, **64**, 2171 (1942).

(12) R. W. Crowe and C. P. Smyth, *ibid.*, **73**, 5406 (1951).

(13) A. H. White and W. S. Bishop, *ibid.*, **62**, 8 (1940).

(14) R. J. Meakins, *Australian J. Chem.*, **6**, 104 (1953).

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mental results are represented in the plots of ϵ' against temperature.

Discussion of Results

Attempts to Form Solid Solutions.—In order to separate the hydroxyl groups in alcohols from one another so that the transfer of a proton from one molecule to the next would be impossible, attempts were made to form solid solutions of tetradecyl alcohol and hexadecyl alcohol in dicetyl ($C_{32}H_{66}$) and in hexadecyl ether. These solvents were selected as having molecules of approximately the same length as the associated double molecules of the alcohols and thus providing lattices into which the alcohol molecules should fit. Curves for the pure compounds were first obtained. The one for dicetyl is reproduced in Fig. 1. The increase in dielectric constant from 2.05 to 2.24 at 69.2° is due to an increase in density upon freezing. A phase transition, which occurs at 64.3° on cooling and at 64.6° on warming, is also clearly shown by a discontinuity in the dielectric constant–temperature curve. The drop in dielectric constant is probably due to a constraint upon the vibrations of the nuclei in the low temperature form of the compound. The dielectric constant–temperature curve for carbon tetrachloride, which is inserted in Fig. 1 for comparison, also shows a drop in dielectric constant at its phase transition. Cooling curves for the two alcohols, Figs. 2 and 3, are substantially the same as those previously obtained.[4,6]

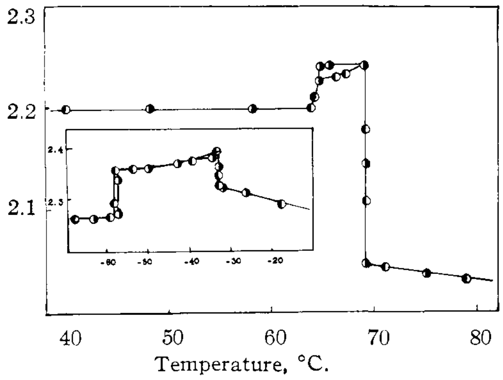

Fig. 1.—Variation of the dielectric constants of dicetyl and carbon tetrachloride (inset) with temperature. Left-half filled circles are for cooling, and right-half filled circles are for warming.

In Fig. 4 is shown the dielectric constant of a sample of dicetyl containing 9.6% cetyl alcohol. The breaks in the curve occurring at 68.2 and 64.5° correspond to the freezing and transition points of dicetyl. At 48.2° there is another discontinuity in the curve, and the dielectric constant becomes frequency dependent. This temperature corresponds to the freezing of the alcohol into its rotator phase. The dielectric behavior of the solid clearly shows the properties characteristic of both solid dicetyl and solid cetyl alcohol, indicating their presence as two distinct solid phases. A similar interpretation must be given to the data obtained for the tetradecanol–dicetyl mixture, which is plotted in Fig. 5. The warming curves for these mixtures (not shown) are similar to the cooling curves except that the transition in the alcohol phase is virtually missing, as is also the case in the pure alcohols.[4,6]

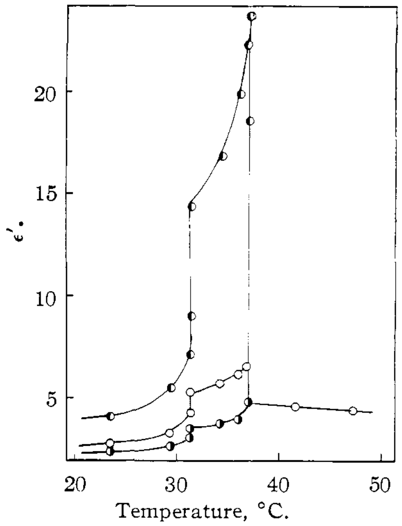

Fig. 2.—Variation of the dielectric constant of tetradecanol with decreasing temperature. Left-half filled circles represent values obtained at 0.5 kc., hollow circles at 5 kc., and right-half filled circles at 50 kc.

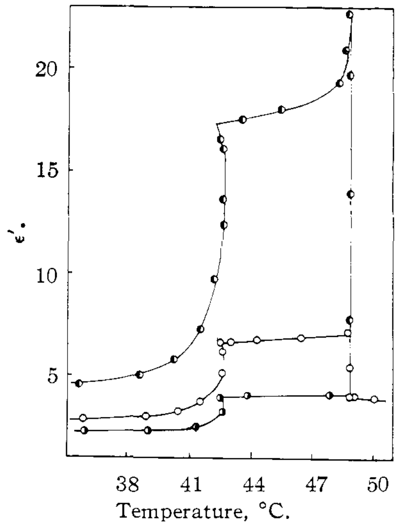

Fig. 3.—Variation of the dielectric constant of hexadecanol with decreasing temperature. Left-half filled circles represent values obtained at 0.5 kc., hollow circles at 5 kc., and right-half filled circles at 50 kc.

A mixture of 7 mole % tetradecanol with hexadecyl ether also failed to form a solid solution. The curve (Fig. 6) is slightly complicated by the fact that the ether has a dispersion region of its own in the same temperature range as the alcohol.[16] The effect of the alcohol may be seen, however, by comparing the maximum values for the dielectric constant in the mixture, which is over 8 at 0.5 kc., with the corresponding point, 5.3, in pure hexadecyl ether. Despite this complicating feature, hexadecyl ether was chosen in preference to dodecyl or tetradecyl ether as solvent because the melting points of the latter are rather low, so that, if a solid

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[16] A. Di Giacomo and C. P. Smyth, THIS JOURNAL, **78**, 2027 (1956).

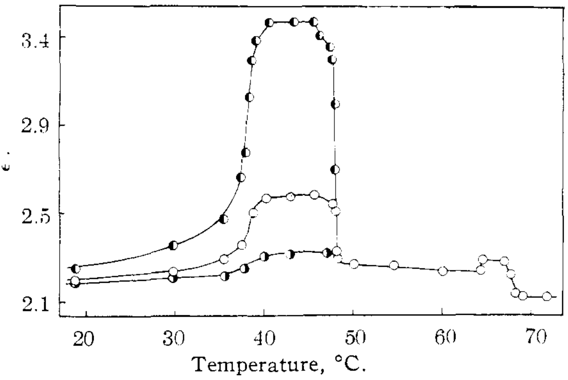

Fig. 4.—Variation of the dielectric constant of a mixture of 9.6 mole % hexadecanol in dicetyl with decreasing temperature. Left-half filled circles represent values obtained at 0.5 kc., hollow circles at 5 kc., and right-half filled circles at 50 kc.

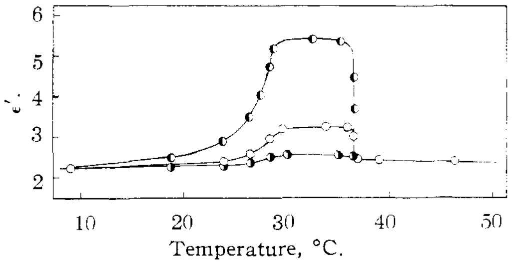

Fig. 5.—Variation of the dielectric constant of a mixture of 24 mole % tetradecanol in dicetyl with decreasing temperature. Left-half filled circles represent values obtained at 0.5 kc., hollow circles at 5 kc., and right-half filled circles at 50 kc.

solution between the alcohol and these ethers were realizable, it might form at a temperature below the range in which the α-form of the alcohol was stable, which would defeat the purpose of the experiment.

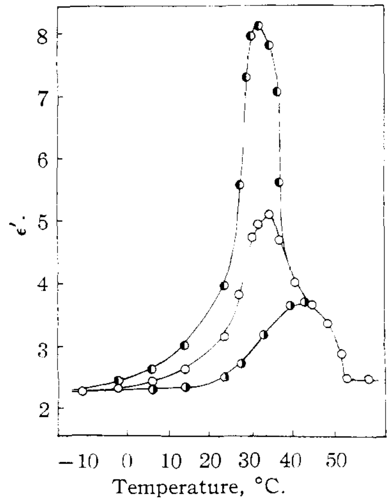

Fig. 6.—Variation of the dielectric constant of a mixture of 7 mole % tetradecanol in hexadecyl ether with decreasing temperature. Left-half filled circles represent values obtained at 0.5 kc., hollow circles at 5 kc., and right-half filled circles at 50 kc.

Although the attempts to form solid solutions and thereby prevent proton transfer were unsuccessful, the reproducibility of the anomalous behavior of the long-chain alcohols is of interest.

Long-chain Mercaptans.—It was evident from the time dependence of the dielectric constant of the solid, from the differences betweeen the melting point and the freezing point, and from the fact that the melting point was higher the longer the solid was stored, that in both tetradecyl mercaptan and octadecyl mercaptan, the solid phase initially formed was not stable. In Fig. 7 are plotted a cooling curve for octadecyl mercaptan and warming curves for samples of this compound of various thermal histories. The liquid froze sharply at 27.6° with a drop in dielectric constant. With a sample that was re-warmed immediately there was evidence of partial melting at the freezing point, but, because of an irreversible transformation to a stable modification, most of the sample melted a few degrees higher. The solid was maintained at room temperature for several days, during which time its dielectric constant dropped to the low value of 2.5. The melting point of a sample so treated was 30.5°. The corresponding curves for tetradecyl mercaptan are shown in Fig. 8. The liquid froze sharply at 3.3° and upon immediate rewarming melted about 1° higher. Complete transformation to the stable form was effected by storing the cell with the compound in it in an ice-bath for several days.

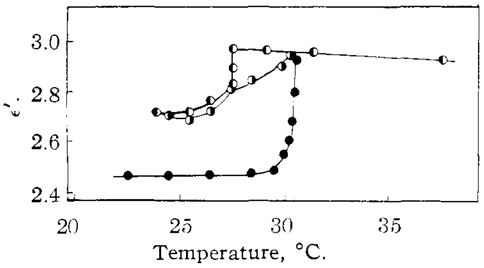

Fig. 7.—Variation of the dielectric constant of octadecyl mercaptan with temperature. Filled circles are for warming of stable form. Left-half filled circles represent cooling from melt, and right-half filled circles, immediate rewarming of sample.

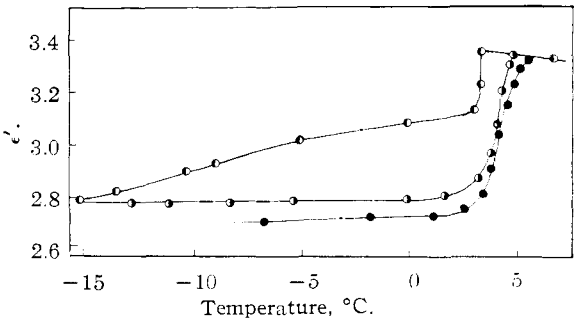

Fig. 8.—Variation of the dielectric constant of tetradecyl mercaptan with temperature. Filled circles are for warming of stable form. Left-half filled circles represent cooling from melt, and right-half filled circles, immediate rewarming of sample.

The metastable (rotator) phases of the mercaptans were obtained by plunging the melt into a mixture of Dry Ice and acetone; the samples were then cooled to liquid nitrogen temperature, and warming runs taken. Curves for these measurements are given in Figs. 9 and 10 for octadecyl and tetradecyl mercaptan, respectively. It is clear from the figures that dipole orientation is possible in the α-phase of these compounds. Unfortunately, the dispersion region was spread out over so wide a frequency range that it was not possible to obtain accurate loss measurements. Above the dispersion region, where measurement at 5 kc. corresponds to the static dielectric constant, the dielectric constant began to drop with increasing temperature, as it should, if molecular rotational orientation were occurring. The appearance of the low temperature dispersion region is reminiscent of that observed in the α-forms of the triglycerides[8,9,17] where rotation of the molecule as a whole is presumably prevented by its shape, and only that of segments should be permitted, and also of that in the long-chain fatty acid esters,[18] where rotation of the molecule around its long axis appears possible. Dispersion below the melting point with rise in dielectric constant above that of the liquid is commonly attributable to interfacial polarization[19] between a solid phase and a more or less conducting liquid phase arising from the presence of impurities, but this behavior is not shown by the stable forms in Figs. 7 and 8. Impurities do not, therefore, appear to be the cause of the dispersion. Possibly, enough weak hydrogen bonding occurs between the mercaptan molecules in a rotator phase to give a very small effect analogous to that which is so conspicuous in the behavior of the hydrogen-bonded alcohols. However, it is clear that strong hydrogen bonding is necessary to produce the effect observed in the long-chain alcohols.

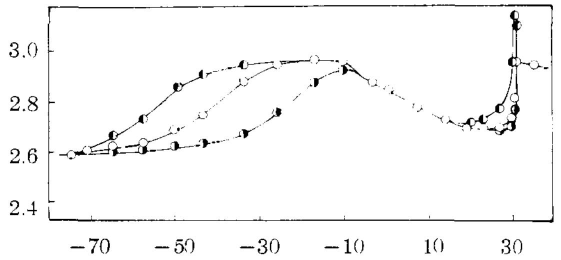

Fig. 9.—Variation of the dielectric constant of the α-form of octadecyl mercaptan with increasing temperature. Left-half filled circles represent values obtained at 0.5 kc., hollow circles at 5 kc., and right-half filled circles at 50 kc.

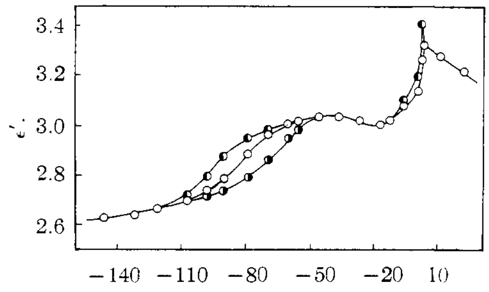

Fig. 10.—Variation of the dielectric constant of the α-form of tetradecyl mercaptan with increasing temperature. Left-half filled circles represent values obtained at 0.5 kc., hollow circles at 5 kc., and right-half filled circles at 50 kc.

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[17] R. W. Crowe and C. P. Smyth, THIS JOURNAL, **73**, 2040 (1951).

[18] R. W. Crowe and C. P. Smyth, *ibid.*, **73**, 5401 (1951).

[19] C. P. Smyth, ref. 8, p. 73.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XIV. The Apparent Critical Wave Lengths of Liquid Long Chain Alcohols[1]

BY G. B. RATHMANN,[2] A. J. CURTIS, P. L. MCGEER AND C. P. SMYTH

RECEIVED OCTOBER 6, 1955

The dielectric constants and losses of *t*-butyl, octyl, decyl, dodecyl, tetradecyl, cetyl and octadecyl alcohols and of solutions of decyl alcohol in carbon tetrachloride and in nujol have been measured at wave lengths at 1.25, 3.22 and 10.0 cm. at temperatures between 2 and 85°. Approximate critical wave length values calculated from the results of these measurements are shown to be consistent with the explanation of measurements on shorter chain alcohols by other investigators as involving a low frequency dispersion region arising from hydrogen bonds and a high-frequency region arising from the rotational orientation of alkoxy groups.

The microwave measurements reported in the present paper were carried out some six years ago with the expectation that further measurements would be carried out at somewhat lower frequencies. Although these projected lower frequency measurements have not been carried out in this Laboratory, much additional information has been obtained elsewhere on alcohols up to dodecyl in size. It has, therefore, seemed desirable to publish the present results in spite of the fact that absence of data at wave lengths of a few meters leaves the calculated critical wave length values very approximate.

Earlier papers[3-6] in this series have described the

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[1] This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] This article is based upon a thesis submitted by Dr. G. B. Rathmann in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

[3] W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, THIS JOURNAL, **70**, 4093 (1948).

[4] H. L. Laquer and C. P. Smyth, *ibid.*, **70**, 4097 (1948).

[5] W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3443 (1950).

[6] F. H. Branin, Jr., and C. P. Smyth, *J. Chem. Phys.*, **20**, 1121 (1952).