JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

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VOLUME 78 MAY 21, 1956 NUMBER 10

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Dipole Orientational Freedom in Certain Solid Long-chain Ethers and Triglycerides[1]

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

RECEIVED OCTOBER 26, 1955

The dielectric constants and losses of eight substances with long molecules have been measured at frequencies between 0.25 and 100 kilocycles over a wide range of temperature in the liquid and solid states. Dodecyl and tetradecyl ethers showed no molecular orientational freedom in the solid state, while hexadecyl and octadecyl ethers in the solid state had abnormally high dielectric constants with wide dispersion regions corresponding to a wide distribution of relaxation times. 1-Oleyldipalmitin and 1-oleyldistearin showed the complex polymorphism characteristic of triglycerides, some of the solid phases having dielectric constants as large as or larger than the liquids. The α-phase, in particular, showed a wide region of anomalous dispersion. Because of the large size and irregular shape of the molecules, it would appear that dipole orientation must arise from the motion of segments rather than of the molecule as a whole. Stearamide showed no molecular rotational freedom in the solid state. Cholesteryl stearate showed an apparent hysteresis of about 1° between its melting and freezing points with no dipole orientation below either and no discontinuity corresponding to a transition between the solid and the smectic state.

It has been known for some time that certain long chain molecules may assume a state of "free" rotation about their long axes in the solid state. This phenomenon (or its absence) has been investigated[4] in long chain paraffins, alcohols, amines, esters, bromides, ketones and glycerides. Investigations of four long-chain ethers, two triglycerides, stearamide and cholesteryl stearate are reported in the present paper.

Materials and Experimental Method

The dielectric constants ϵ' and loss factor ϵ'' were measured at various frequencies from 0.25 to 100 kilocycles by means of the impedance bridge previously described.[5,6] The experimental results are represented in the plots of ϵ' and ϵ'' against temperature.

The ethers, obtained from The Matheson Company, were purified by vacuum distillation followed by repeated crystallizations from methanol-benzene solution. Their melting points are compared with literature values in Table I.

TABLE I

MELTING POINTS OF LONG-CHAIN ETHERS

	M.p., °C. This work	M.p., °C. Lit.[7]
$(C_{12}H_{25})_2O$	31.2	33
$(C_{14}H_{29})_2O$	43.3	38.4
$(C_{16}H_{33})_2O$	52.0	54
$(C_{18}H_{37})_2O$	59.4	58-60

Pure samples of 1-oleyldipalmitin and 1-oleyldistearin were kindly lent to us by the Procter and Gamble Company, Ivorydale, Ohio.

Discussion of Results

Ethers.—Figure 1 contains two curves for dodecyl ether, one obtained with a sample which had been twice distilled only, and the other with a sample which had been further purified by extensive crystallization. The two curves strikingly illustrate the effect of impurities upon the dielectric constant of a solid as a function of temperature. The dielectric constant of the less pure sample rises appreciably with increasing temperature, does not show a sharp break at the melting point, and has too high a value in the liquid state. The smaller slope observed in the ϵ' *vs.* T curve of the second sample may be attributable to small amounts of impurities still remaining in it or to a trace of dipole orientational freedom, which increases with rising tempera-

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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] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, Chap. V, Sect. 4.

[5] C. P. Smyth and C. S. Hitchcock, THIS JOURNAL, **54**, 4631 (1932); **55**, 1830 (1933).

[6] J. D. Hoffman and C. P. Smyth, *ibid.*, **71**, 431 (1949).

[7] A. W. Ralston, "Fatty Acids and Their Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 759.

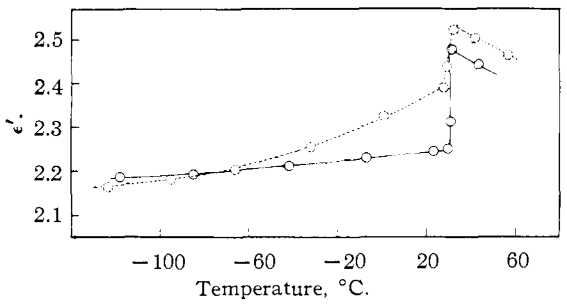

Fig. 1.—Variation of the dielectric constant of dodecyl ether with temperature. Dotted line represents the curve obtained with an impure sample.

ture. From the drop in dielectric constant upon freezing, and the absence of frequency dependence in the solid, it must be concluded that in crystalline dodecyl ether, the molecules are frozen rigidly into place so that the permanent dipoles can make no appreciable contribution to the dielectric constant of the material. Figure 2 shows that tetradecyl ether also possesses no appreciable amount of molecular orientational freedom in the solid state.

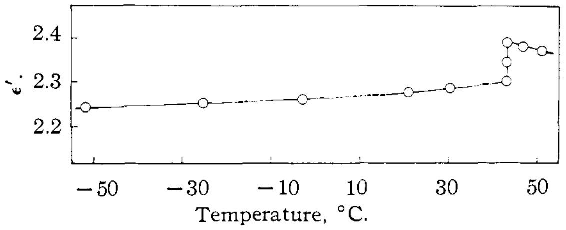

Fig. 2.—Variation of the dielectric constant of tetradecyl ether with temperature.

The dielectric constants of hexadecyl and octadecyl ethers (Figs. 3 and 4) differ markedly from those of the two lower members of the series. The fact that freezing is accompanied by a rise in dielectric constant due to the density increase accompanying the phase change indicates freedom of dipole orientation in the solid. The ethers do not show a transition to a non-rotator phase. When cooled, the dielectric constant goes through a region of anomalous dispersion. At temperatures below about −20° the relaxation time has become so large that the dipoles are unable to orient themselves in the applied field even at a frequency of 500 cycles per second. The dielectric constants of hexadecyl and octadecyl ethers at these low temperatures are comparable to those of the non-rotating dodecyl and tetradecyl ethers.

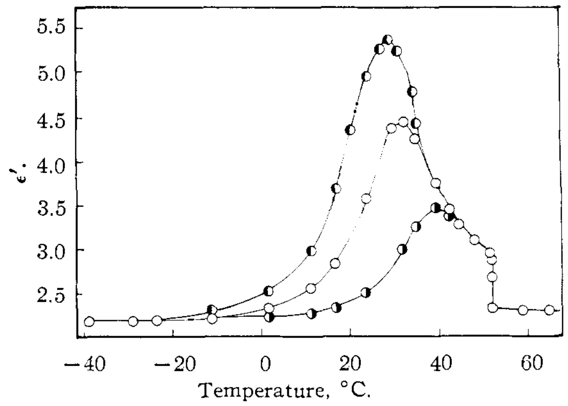

Fig. 3.—Variation of the dielectric constant of hexadecyl ether with temperature. Left-half filled circles represent values obtained at 0.5 kc., and right-half filled circles at 50 kc.

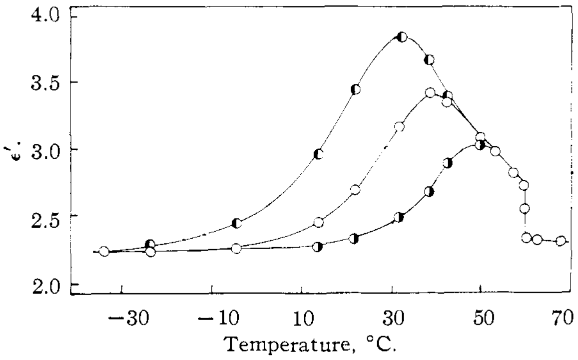

Fig. 4.—Variation of the dielectric constant of octadecyl ether with temperature. Left-half filled circles represent values obtained at 0.5 kc., hollow circles at 5 kc., and right-half filled circles at 50 kc.

In having a dispersion region just below the freezing point and in failing to show a rotational transition, these two ethers resemble the long-chain esters, *n*-decyl palmitate and *n*-hexadecyl palmitate.[8] However, while the dielectric constant of *n*-decyl palmitate decreases slightly with decreasing temperature before the drop caused by dispersion sets in and that of *n*-hexadecyl palmitate increases at about the same rate as that shown by the liquid, the dielectric constants of the two ethers increase much more rapidly in the solid than in the liquid state, attaining anomalously high values. Anomalously high values found[6] for long-chain alcohols in a rotator state were attributed to the migration of protons involved in hydrogen bonding, which also produced very high losses. The absence of ionizable hydrogens eliminates any such explanation for the behavior of the ethers. The absence of any similar anomaly in the behavior of the two shorter ethers as well as its considerable size would seem to rule out the remote possibility that the effect might arise from the presence of a trace of methyl alcohol from the solvent from which the solid alcohols were crystallized in the process of purification. The behavior of the ether molecules in the liquid state appears to be normal in that calculation of approximate molecular dipole moment values by means of the Onsager equation gives values in reasonable agreement with the values observed for other ethers.[9] X-Ray analysis has shown that the crystals of *n*-hexadecyl ether[10] are monoclinic, which would result in different dielectric constant values along the three different axes. It is possible that, in the process of crystallization of the long-chain ether molecules in the narrow space between the cylinders of the measuring condenser, some preferential orientation of the crystals occurred so as to place the axis of largest dielectric constant perpendicular

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(8) R. W. Crowe and C. P. Smyth, THIS JOURNAL, **73**, 5401 (1951).

(9) C. P. Smyth, ref. 4, p. 298.

(10) R. Kohlhaas, *Ber.*, **73B**, 189 (1940).

to the cylinder faces, but the effect of such orientation should be less than the observed apparent elevation of dielectric constant. It is also remotely possible that the packing of the long chains parallel to one another in the crystal lattice with the oxygens in parallel sheets may give rise to some coöperative dipole orientation with resultant increase in the average dielectric constant.

The frequency dependence of the dielectric constant and loss was determined at each of several temperatures for hexadecyl ether and octadecyl ether. Typical curves are shown in Figs. 5 and 6, which also include Cole and Cole arc plots of dielectric constant *vs.* loss at different frequencies. The relaxation time, τ, at each temperature was calculated from the expression $\tau = {}^1/_{2\pi f_m}$, where f_m, the critical frequency, was determined by graphical interpolation. Log $(1/\tau)$ is plotted against $1/T$ for both ethers in Fig. 7, and $\Delta H^{\ddagger}$, the heat of activation, and $\Delta S^{\ddagger}$, the entropy of activation, are calculated.[11] These quantities are tabulated in Table II, together with those of the distribution parameter, α.

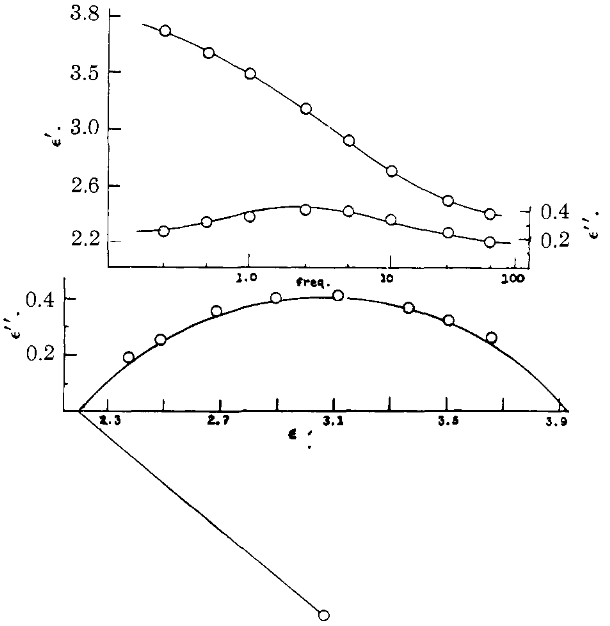

Fig. 5.—Dispersion data for hexadecyl ether at 22°: *top*, dielectric constant and dielectric loss *vs.* frequency (in kc.) plotted logarithmically; *bottom*, arc plot of dielectric loss *vs.* dielectric constant.

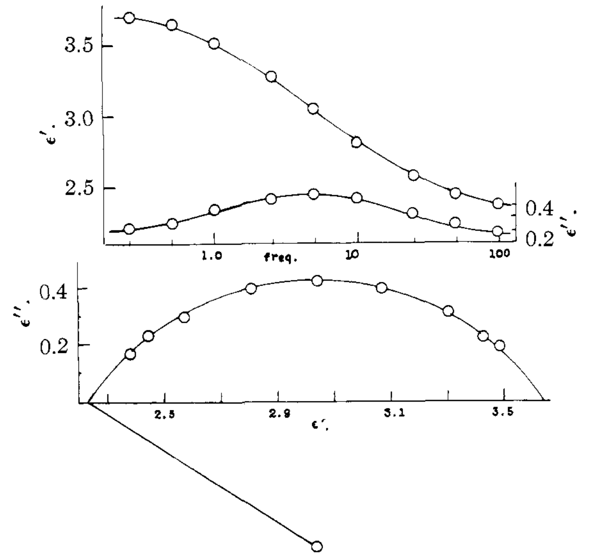

Fig. 6.—Dispersion data for octadecyl ether at 29.5°: *top*, dielectric constant and dielectric loss *vs.* frequency (in kc.) plotted logarithmically; bottom, arc plot of dielectric loss *vs.* dielectric constant.

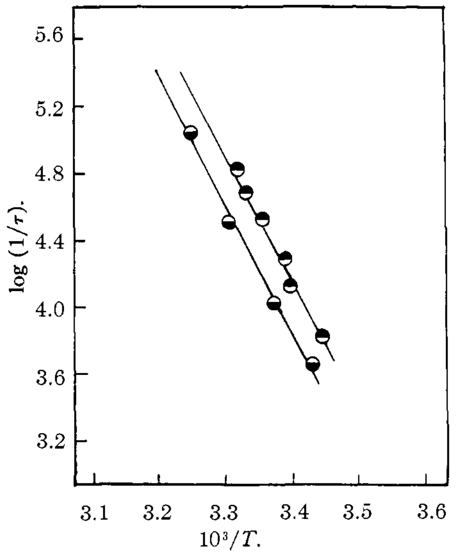

Fig. 7.—Briggsian logarithm of reciprocal relaxation time *vs.* reciprocal temperature. Top-half filled circles are for hexadecyl ether; bottom-half filled circles are for octadecyl ether.

TABLE II

ENERGIES AND ENTROPIES OF ACTIVATION AND DISTRIBUTION CONSTANTS FOR ETHERS

t, °C.	α	$\tau \times 10^6$	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
		$(C_{16}H_{33})_2O$	35	78
17.8	0.54	159		
21.2	.50	80.0		
22.0	.44	54.6		
25.0	.38	31.4		
27.3	.38	21.7		
28.3	.32	15.6		
		$(C_{18}H_{37})_2O$	36	78
18.6	0.46	236		
23.6	.44	100		
29.5	.37	31.7		
34.7	.39	12.0		

It is seen in Figs. 5 and 6 that the dielectric behavior of these solid ethers departs greatly from that predicted by the simple Debye theory, which requires that most of the dispersion occur in two logarithmic decades and that ϵ'' plotted against ϵ' yield a semi-circle with its center on the ϵ' axis.

In spite of differences in behavior, there is an interesting parallelism between the long-chain ethers and the long-chain alcohols. In the ethers,

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[11] See S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, Chap. IX.

rotational orientation is not observed for the dodecyl and tetradecyl compounds, but occurs when the chain length is increased to that of hexadecyl and octadecyl. Rotational orientation appears to set in with n-tetradecyl alcohol and continue in the longer-chained alcohols.[4,6] End-to-end association of the alcohol molecules by hydrogen bonding makes double tetradecyl alcohol molecules in the crystal lattice of about the same over-all chain length as the hexadecyl ether molecules. n-Hexadecyl palmitate, $C_{15}H_{31}COOC_{16}H_{33}$, has almost the same molecular dimensions and almost the same unit cell dimensions in its monoclinic lattice[12] as has n-hexadecyl ether. Although both solids show dipole orientational freedom, the ether (Table III) has, at approximately the same temperature, much the larger distribution of relaxation times, much the higher most probable relaxation time, and considerably larger values for the heat and entropy of activation. This behavior would be consistent with the existence of a coöperative effect suggested as possibly the cause of the anomalously high dielectric constants of the solid hexadecyl and octadecyl ethers. Both compounds show a more rapid decrease in the value of the distribution parameter with rising temperature than that commonly observed for liquids.

TABLE III

COMPARISON OF QUANTITIES FOR ETHER AND ESTER[8]

	α	$\tau \times 10^6$ (sec.)	$\Delta H^{\mp}$, kcal./mole	$\Delta S^{\mp}$, e.u.
$C_{16}H_{33}OC_{16}H_{33}$	0.50(21.2°)	80.0(21.2°)	35	78
$C_{15}H_{31}COOC_{16}H_{33}$	.16(19.8°)	6.62(19.8°)	21	36

Triglycerides.—The dielectric properties of the 1-mono-, 1,3-di-, simple tri-, and symmetrical mixed triglycerides of oleic, palmitic and stearic acids have previously been investigated in this Laboratory.[4] These data, together with thermal and X-ray diffraction studies, have shed light upon the interesting and sometimes peculiar polymorphic behavior of glycerides.

On slow cooling of 1-oleyldipalmitin, OPP, (Fig. 8) the sample remained liquid until a temperature of 18.1°, which corresponds to the melting point (18.5°) of the α-form as determined by a "thrust in" technique.[13] At 18.1° the α-form, which, presumably, forms initially from the melt, was immediately transformed to the stable β-form with the evolution of heat. The sample spontaneously warmed up faster than its surroundings to about 24° and then cooled down again. During this time, the dielectric constant dropped continuously from a value of 3.13 to 2.45. Upon immediate rewarming, the solid melted at about 32.8°. When the stable form of OPP was stored in the dielectric cell for a day, its dielectric constant fell to about 2.35 as the α-β transformation became more nearly complete. A sample treated in this way melted at 33.8°, whereas one stored for one week at 32° was reported[13] to melt at 34.8°. Allotropically pure crystals of the stable form, β-3, obtained by crystallization from acetone, melted at 35.2°.[13]

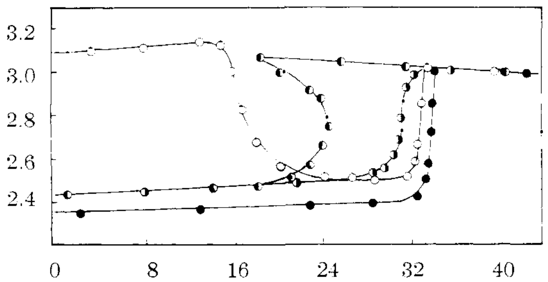

Fig. 8.—Variation of the dielectric constant of 1-oleyldipalmitin with temperature. Hollow circles are for warming of α-phase, filled circles for warming of stable form. Left-half filled circles represent cooling from melt, and right-half filled circles, immediate rewarming of sample.

The α-form of 1-oleyldistearin, OSS, (Fig. 9) is stable enough to be obtained by cooling the liquid to 30.1°. On warming, however, it did not melt at this temperature, but instead underwent a transformation to the β-form with evolution of heat and a decrease in the dielectric constant of the sample from 3.0 to 2.5. The β-form, or rather, a mixture of β with some α, melted at 40°. An allotropically purer sample of β-OSS, obtained by prolonged storage of the sample had a dielectric constant of 2.25, and melted at about 41°. Lutton[13] reports that crystals of β-3 obtained from acetone melt at 43.5° and that a chilled sample maintained at 38° for one week melted at 42.5°.

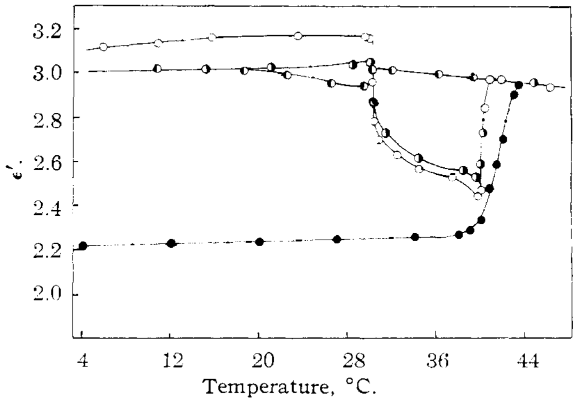

Fig. 9.—Variation of the dielectric constant of 1-oleyldistearin with temperature. Hollow circles are for warming of α-phase, filled circles for warming of stable form. Left-half filled circles represent cooling from melt, and right-half filled circles, immediate rewarming of sample.

The α-forms of these unsymmetrical triglycerides were obtained by plunging the cell containing the melt into an ice-bath and then cooling to liquid nitrogen temperature. Warming runs were then taken. The data are represented in Figs. 10 and 11 for 1-oleyldipalmitin and 1-oleyldistearin, respectively. In general shape, the dielectric constant *vs.* temperature curves of the α-forms of these two triglycerides are very similar to the corresponding curves of other triglycerides.[14] The dielectric constant is approximately equal to the square of the

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[12] R. Kohlhaas, *Z. Krist.*, **98**, 418 (1938).

[13] E. S. Lutton, THIS JOURNAL, **73**, 5595 (1951).

[14] R. W. Crowe and C. P. Smyth, *ibid.*, **72**, 528 (1950); **73**, 2040 (1951).

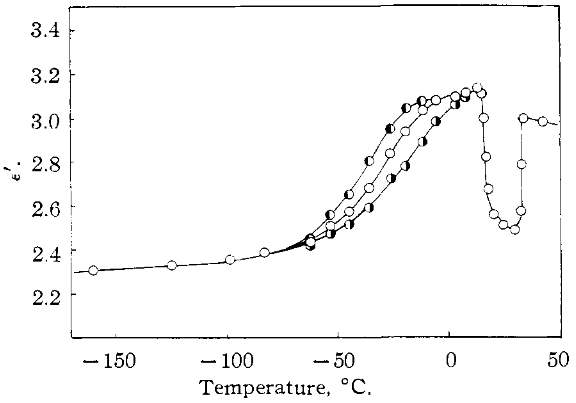

Fig. 10.—Variation of the dielectric constant of the α-form of 1-oleyldipalmitin with increasing temperature. Left-half filled circles represent values obtained at 0.5 kc., hollow circles at 5 kc., and right-half filled circles at 50 kc.

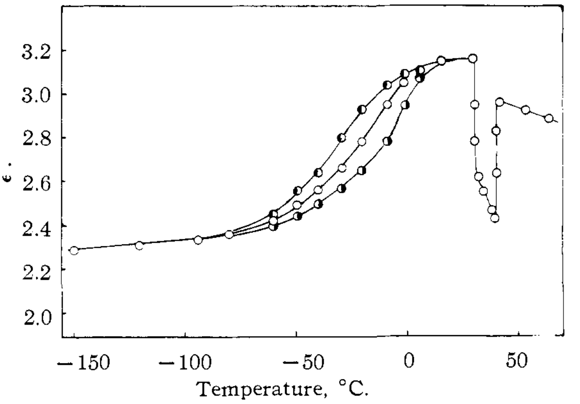

Fig. 11.—Variation of the dielectric constant of the α-form of 1-oleyldistearin with increasing temperature. Left-half filled circles represent values obtained at 0.5 kc., hollow circles at 5 kc., and right-half filled circles at 50 kc.

refractive index at very low temperatures. At higher temperatures, the permanent dipoles begin to contribute to the dielectric constant, which rises and becomes frequency dependent. The dispersion is spread out over many logarithmic decades indicating a wide distribution of relaxation times. Near the α-melting point, the dielectric constant is slightly higher than it is in the liquid, showing that the dipole orientational freedom in the α-phase is comparable to what it is in the liquid.

As has been noted, upon heating, the α-form of a triglyceride, instead of melting, is transformed to a more stable form of lower dielectric constant, which melts a few degrees higher. Figures 8 and 9 show this phenomenon quite clearly for the unsymmetrical triglycerides, since there is only one β-form and, therefore, no complicating features appear, in contrast to the dielectric constant *vs.* temperature curve of the symmetrical 2-oleyldipalmitin, which exists in four crystalline forms,[15] or that for 2-oleyldistearin which exists in three forms.[14] The melting point of the most stable form of 1-oleyldistearin was found to be about 40°, quite close to that of the isomeric 2-oleyldistearin, 43.5°. Hydrogenation of the double bond in the oleyl radical transforms either of the above to tristearin, SSS, the melting point of whose stable form is 73°. That the large difference between the melting points of SOS and SSS may be correlated with observed differences in crystal structure already has been noted.[14] The observation logically extends itself to the unsymmetrical OSS.

Stearamide.—In Fig. 12 is plotted the dielectric constant of a sample of stearamide prepared by bubbling ammonia gas into stearoyl chloride. The low value of its dielectric constant, 2.2 at temperatures below 70° show that no rotational freedom exists in solid stearamide. The apparent dielectric constant and the conductivity rose tremendously, however, as the melting point was approached, so that it became impossible to balance

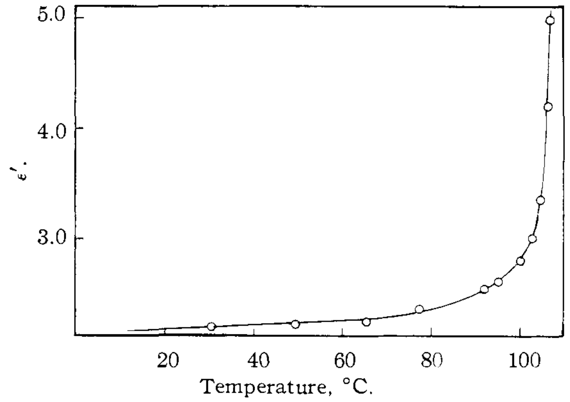

Fig. 12.—Variation of the dielectric constant of stearamide with temperature.

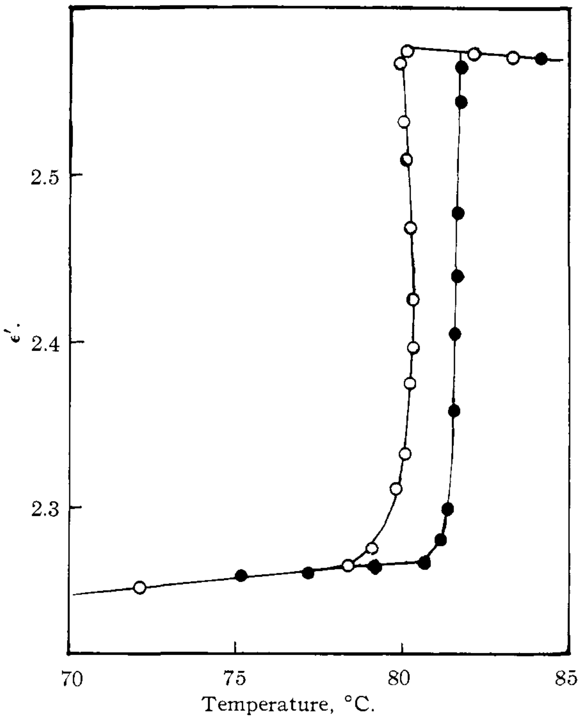

Fig. 13.—Variation of the dielectric constant of cholesteryl stearate with temperature. Hollow circles are for cooling run, and filled circles are for warming run.

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[15] E. S. Lutton and F. J. Jackson, THIS JOURNAL, **72**, 3254 (1950).

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 $\rightleftarrows$ liquid crystal) for cholesteryl stearate as 78°, and the melting point (liquid crystal $\rightleftarrows$ 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

(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).

(15) C. P. Smyth and C. S. Hitchcock, THIS JOURNAL, **54**, 4631 (1932); **55**, 1830 (1933).