[Contribution from the Frick Chemical Laboratory, Princeton University]

Molecular Rotation in Some Long-chain Fatty Acid Esters in the Solid State[1,2]

By Robert W. Crowe[3] and Charles P. Smyth

Five long-chain alkyl esters of palmitic and stearic acids have been synthesized and carefully purified. Their dielectric constants and losses have been investigated over a wide temperature range at frequencies from 0.5 to 100 kilocycles. *n*-Decyl palmitate, *n*-dodecyl stearate and *n*-hexadecyl palmitate possess high dielectric constants below their freezing points, indicating freedom of dipole orientation, probably about the long molecular axis. The orientation process involves a small distribution of relaxation times, the extent of the distribution increasing with decreasing temperature. The marked increase in relaxation time with increase in chain-length, together with the small distribution, supports the current views that long-chain molecules orient as a whole by rotation about their chain axes in the solid state. Energies and entropies of activation for the orientation process have been calculated for the esters. A sharp drop in the dielectric constants of *n*-dodecyl palmitate and *n*-tetradecyl stearate upon solidification indicates an absence of molecular freedom in the crystals. Dielectric constant measurements on ethylene dimyristate, ethylene dipalmitate and ethylene distearate show that their molecules are held rigidly in the crystal lattice, and are unable to orient below the freezing point. The dielectric behavior of *n*-octadecyl acetate, the α form of which shows a considerable amount of orientational freedom, has been compared with its previously investigated isomer, ethyl stearate. Measurements on a very pure sample of stearic acid show a sharp peak at the freezing point like those previously observed for this and other long-chain acids. Due to its strong tendency to form non-polar dimers, the dielectric properties of this compound resemble closely those of a long-chain hydrocarbon.

The possibility of molecular orientational freedom about the long molecular axis has been investigated in polycrystalline long-chain alcohols,[4-6] bromides,[7] symmetrical ketones[8] and a few long-chain aliphatic esters.[4,9] 1-Monopalmitin and 1-monostearin[10] were found to possess molecular freedom in the metastable α-forms. Dielectric constant and loss measurements were, however, complicated by an abnormally high electrical conductivity and strong frequency-dependence of the dielectric constant, similar to that observed for the long-chain alcohols.[6] These phenomena were attributed to a proton-transfer mechanism through the sheets of hydroxyl groups in the crystals, giving rise to spatial or interfacial polarization. The α-forms of completely esterified tripalmitin and tristearin[11] were found also to possess dipole orientational freedom, the process being attributed to that of molecular segments because of the unusually wide distribution of relaxation times observed. The tuning fork structure reported for these triglycerides[12] supports this conclusion since rotation of the molecules as a whole would require too large a volume.

The simple long-chain alkyl esters of the fatty acids possess no free hydroxyl groups to give rise to proton transfer, and their molecules probably extend themselves in single, parallel, zig-zag chains in the crystals.[13,14] It has seemed of interest, therefore, to investigate these esters and three esters of ethylene glycol as functions of temperature and frequency in an effort to determine whether the entire hydrocarbon chain is involved in the possible orientation processes or whether orientation may also occur by twisting around the bonds of the molecule as has been suggested by microwave measurements on a number of long-chain liquid alkyl halides.[15]

Preparation and Purification of Materials

The simple alkyl esters of palmitic and stearic acid were synthesized in this Laboratory in the following manner: High grade palmitic and stearic acid from the Matheson Company were first converted to the acyl chloride by the dropwise addition of thionyl chloride. These acyl chlorides were then fractionally distilled twice under reduced pressure. Esterification was carried out by the dropwise addition of acyl chloride to a solution of the desired long-chain alcohol in dry pyridine. The alcohols were also initially purified by fractional distillation under reduced pressure. The crude esters were purified by from five to ten fractional crystallizations from ether–methanol solution. Finally, the purified crystals were placed in a vacuum desiccator for 24 hours to remove traces of moisture and solvent.

Ethylene dimyristate, ethylene dipalmitate and ethylene distearate were obtained from the Eastman Kodak Company. They were purified by five fractional crystallizations from ether–methanol mixture and then dried in a vacuum desiccator.

n-Octadecyl acetate from the Matheson Company was fractionally distilled twice under reduced pressure.

A highly purified sample of stearic acid was kindly given to us by the Procter and Gamble Company. Its dielectric properties were investigated immediately after removal from the vacuum desiccator in which it had been placed for several hours.

In Table II are listed the melting points of the compounds investigated as obtained from dielectric constant measurements. These are compared with reliable literature values where available.

Experimental Method and Results

The dielectric constants ϵ' and loss factors ϵ'' were measured at various frequencies from 0.5 to 100 kilocycles with the aid of the impedance bridge previously described.[6,16] As in previous measurements with this apparatus,[10,11] the average error in determination of the dielectric constant never exceeded ±1%. The specific conductivity was calculated by the equation $k = 0.0885/RC_0$ where R is the resistance of the cell in ohms and C_0 its vacuum capacitance in $\mu\mu$f. From this the loss factor was calculated by using the relation $\epsilon'' = 1.8 \times 10^{12}k/f$, where f is the frequency in cycles/sec. The average rate of warming and cooling was

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(2) This paper represents a part of the work submitted by Mr. R. W. Crowe 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, 1949–1951.

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

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

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

(7) J. D. Hoffman and C. P. Smyth, *ibid.*, **72**, 171 (1950).

(8) A. Müller, *Proc. Roy. Soc.* (*London*), **A158**, 403 (1937).

(9) R. Buckingham, *Trans. Faraday Soc.*, **30**, 377 (1934).

(10) R. W. Crowe and C. P. Smyth, This Journal, **72**, 4427 (1950).

(11) R. W. Crowe and C. P. Smyth, *ibid.*, **72**, 5281 (1950).

(12) E. S. Lutton, *ibid.*, **70**, 248 (1948); C. E. Clarkson and T. Malkin, *J. Chem. Soc.*, 666 (1934).

(13) T. Malkin, *Trans. Faraday Soc.*, **29**, 977 (1933).

(14) Th. Schoon, *Z. physik. Chem.*, **B39**, (1938).

(15) E. J. Hennelly, W. M. Heston and C. P. Smyth, This Journal, **70**, 4102 (1948).

(16) C. P. Smyth and C. S. Hitchcock, *ibid.*, **54**, 4631 (1932); **55**, 1830 (1933).

about 0.2° per minute. Several runs were made for each compound to ensure satisfactory reproducibility.

In Table I are listed a few representative values of the dielectric constants and loss factors of *n*-decyl palmitate, *n*-dodecyl stearate and *n*-hexadecyl palmitate in the solid state with temperature and frequency of measurement. The more complete data for these and the other substances investigated can be found in the graphs. In cases where no frequency dependence of the dielectric constant or loss was observed, values are reported only at 5 kilocycles.

TABLE I

DIELECTRIC CONSTANTS AND LOSS FACTORS OF ESTERS

$f \times 10^3$	19.8° ϵ'	19.8° ϵ''	16.4° ϵ'	16.4° ϵ''	9.0° ϵ'	9.0° ϵ''	5.1° ϵ'	5.1° ϵ''
	n-Hexadecyl Palmitate							
0.5	2.993	0.000	3.001	0.016	2.998	0.098	2.979	0.131
1.0	2.988	.033	2.993	.049	2.963	.147	2.914	.196
2.5	2.975	.078	2.964	.111	2.853	.216	2.744	.248
5.0	2.940	.134	2.900	.176	2.702	.254	2.590	.244
10.0	2.854	.202	2.775	.238	2.551	.236	2.470	.194
25.0	2.654	.250	2.570	.240	2.411	.159	2.377	.120
50.0	2.501	.217	2.443	.184	2.357	.100	2.342	.073
75.0	2.427	.172	2.391	.149	2.339	.067	2.332	.049
	n-Dodecyl Stearate				*n*-Decyl Palmitate			
	20.5°		9.8°		−2.0°		−7.8°	
0.5	3.068	0.000	3.032	...	3.114	0.000	3.090	0.000
5.0	3.063	.057	2.917	.183	3.078	.114	2.963	.212
25.0	2.938	.206	2.581	.229	2.800	.273	2.620	.254
50.0	2.773	.248	2.470	.171	2.627	.233	2.487	.188
75.0	2.660	.234	2.433	.114	...	...	...	...
100.0	2.594	...	2.431	...	2.485	...	2.390	...

TABLE II

MELTING POINTS AND ROTATIONAL FREEDOM OF COMPOUNDS

	M.p., °C. C. & S.	M.p., °C. Lit.[17]	Rotational freedom
$C_{15}H_{31}COOC_{10}H_{21}$	29.3	30	Yes
$C_{15}H_{31}COOC_{12}H_{25}$	38.5	41	No
$C_{17}H_{35}COOC_{12}H_{25}$	42.0		Yes
$C_{17}H_{35}COOC_{14}H_{29}$	50.1		No
$C_{15}H_{31}COOC_{16}H_{33}$	51.0	51.6	Yes
$CH_3COOC_{18}H_{37}$ (α)	30.1	30.25	Yes
(β)	32.6	32.85	No
$C_{17}H_{35}COOC_2H_5$		30.5	Restricted[4]
$(C_{13}H_{27}COO)_2C_2H_4$	61.7		No
$(C_{15}H_{31}COO)_2C_2H_4$	69.1	68.7	No
$(C_{17}H_{35}COO)_2C_2H_4$	75.3	75	No
$C_{17}H_{35}COOH$	69.6	69.6	..

Discussion of Results

Table II indicates the presence or absence of rotational freedom in the solids as indicated by their dielectric behavior.

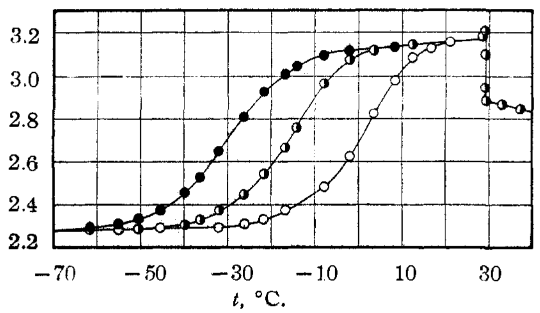

Fig. 1.—The variation of the dielectric constant of *n*-decyl palmitate with decreasing temperature. Hollow circles represent values at 50 kc., half-filled circles values at 5 kc. and filled circles values at 0.5 kc.

Esters of Long-Chain Alcohols.—The variation of the dielectric constant of *n*-decyl palmitate with temperature and frequency is shown graphically in Fig. 1. Upon solidification of the sample, its dielectric constant increased sharply due to an increase in density which resulted in an increase in the amount of polarizable material between the plates of the measuring condenser. This rise indicates that freedom of dipole orientation, comparable to that observed in the liquid, exists in the solid. On further cooling, a region of anomalous dispersion was observed. At temperatures below −60° the relaxation time had increased to such an extent that the orienting dipoles were incapable of following the field even at a frequency of 500 cycles.

The dielectric behavior of solid *n*-dodecyl stearate was similar to that of *n*-decyl palmitate in that full orientation polarization was realized just below the solidification point. A complete examination of its dispersion characteristics in the frequency range employed was somewhat complicated, however, by the appearance of a sharp rotational transition near room temperature, below which rotation was no longer possible. The data in Fig. 2, which are for a warming run, show the transition to be at about 23.5°. When the sample was cooled slowly after solidification, however, it was possible to supercool the rotator phase as much as 15° below this temperature before transformation to the low temperature form began, thus making it possible to investigate its dielectric behavior in the region of maximum loss.* As shown in Table I, rather complete dielectric constant and loss measurements were made upon the rotator phase of this substance at 20.5 and at 9.8°. A small amount of frequency dependence of the dielectric constant observed below the transition temperature (Fig. 2) could arise from incomplete transformation to the low temperature form, since this is apparently a sluggish process.

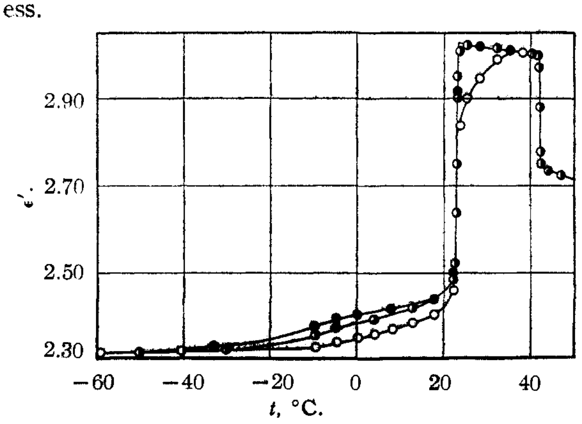

Fig. 2.—The variation of the dielectric constant of *n*-dodecyl stearate with increasing temperature. Hollow circles represent values at 50 kc., half-filled circles values at 5 kc. and filled circles values at 0.5 kc.

The dielectric behavior of *n*-hexadecyl palmitate (Fig. 3) was found to be quite similar to that of *n*-

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(17) A. W. Ralston, "Fatty Acids and Their Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1948, Chaps. I, VII and IX.

* The apparent absence of the transition in *n*-decyl palmitate is undoubtedly the result of even more pronounced supercooling. More extensive investigation has revealed its presence at 10°.

decyl palmitate in that no complicating transitions appeared in the rotator phase. Although the data shown are those for a cooling run, the behavior was found to be entirely reproducible on subsequent warming.

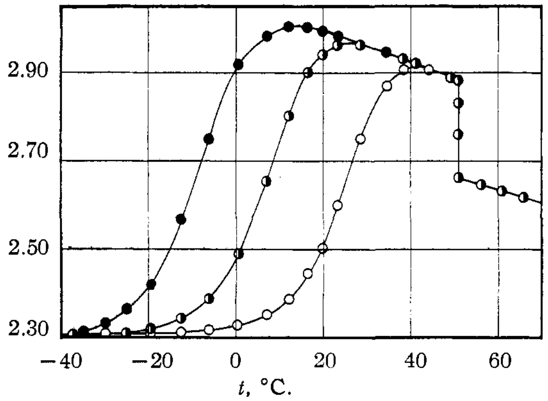

Fig. 3.—The variation of the dielectric constant of *n*-hexadecyl palmitate with decreasing temperature. Hollow circles represent values at 50 kc., half-filled circles values at 5 kc. and filled circles values at 0.5 kc.

The increase in dielectric constant on solidification was greater when these esters were solidified rapidly than when they were allowed to crystallize slowly between the plates of the measuring cell. For example, when an 8-g. sample of *n*-dodecyl stearate was allowed to solidify over a period of two hours, its dielectric constant just below the freezing point was 2.898. When the solidification time was reduced to one-half hour, the dielectric constant assumed a value of 2.998 at the same temperature. That the values attained were a function only of the rate of solidification was indicated by the fact that, after solidification was complete, no decrease was observed with time over a period of 48 hours. The data recorded in Figs. 1, 2 and 3 were obtained for samples which had been allowed to solidify rapidly and represent the maximum values obtained from several runs.

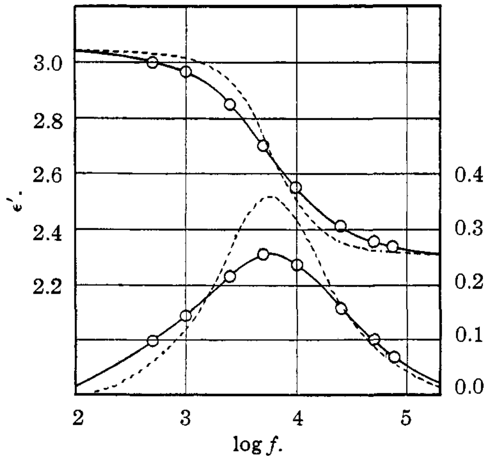

Fig. 4.—The frequency dependence of the dielectric constant and loss factor of *n*-hexadecyl palmitate at 9.0°. Dashed curves represent theoretical behavior assuming single relaxation time and solid curves represent experimental results.

The dependence of dielectric constant and loss upon frequency required by the Debye theory[18] is shown by the dashed curves in Fig. 4. The experimental curves for solid *n*-hexadecyl palmitate in Fig. 4 show departure from ideality, presumably, because of a distribution of relaxation times, which can be expressed by the method of Cole and Cole.[19] A plot of ϵ'' *vs.* ϵ' for different frequencies at a given temperature should give an arc of a circle with its center on the axis. When a distribution of relaxation times is present, the center is depressed below this axis. The angle formed between the ϵ' axis and the line connecting ϵ_∞ with the center of the circle has been designated as $\alpha\pi/2$. Thus α can vary from zero to one and is a measure of the extent of the distribution. Arc plots for *n*-decyl palmitate and *n*-dodecyl stearate are shown in Fig. 5, and for *n*-hexadecyl palmitate in Fig. 6. The three esters evidently possess small but comparable distributions of relaxation times for their orientation processes, as shown by the graphs and by the values of α in Table III.

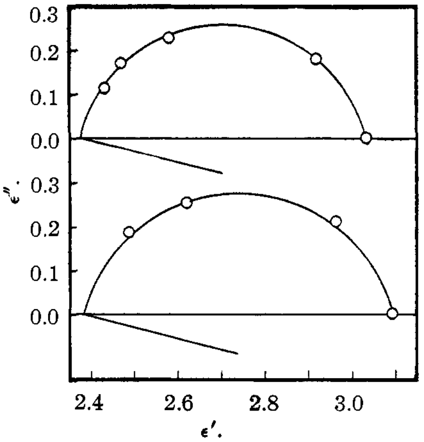

Fig. 5.—Semicircular arc plots for *n*-dodecyl stearate at 9.8° (upper curve) and for *n*-decyl palmitate at −7.8° (lower curve).

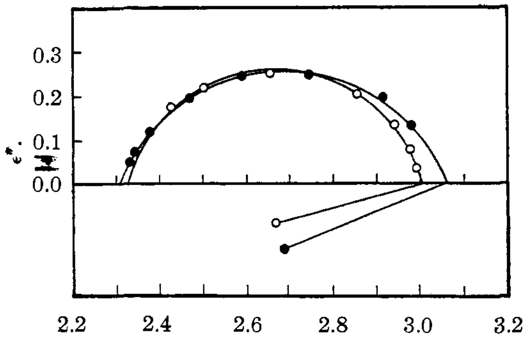

Fig. 6.—Semicircular arc plots for *n*-hexadecyl palmitate at 19.8° (hollow circles) and 5.1° (filled circles).

Investigations in the microwave region on a series of long-chain liquid alkyl chlorides and bromides[15] showed that α was practically zero for

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[18] P. Debye, "Polar Molecules," The Chemical Catalog Co., (Reinhold Publ. Corp.) New York, N. Y., 1929, Chap. V; H. Fröhlich, "Theory of Dielectrics," Oxford University Press, 1949, Sect. 10.

[19] K. S. Cole and R. H. Cole, *J. Chem. Phys.*, 9, 341 (1941).

TABLE III

DISTRIBUTION CONSTANTS AND ACTIVATION ENERGIES AND ENTROPIES FOR ESTERS

Compound	t, °C.	α	$\tau \times 10^6$	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
n-Decyl	−2.0	0.136	6.37	19.3	36.9
palmitate	−7.8	.158	11.4		
n-Dodecyl	20.5	.132	2.90	19.6	33.5
stearate	9.8	.154	10.6		
n-Hexadecyl	19.8	.158	6.62		
palmitate	16.4	.177	9.95	20.7	35.8
	9.0	.227	26.5		
	5.1	.253	49.0		

those molecules which approached spherical symmetry, but increased significantly with increase in the length of the hydrocarbon chain, and with decrease in temperature as in Table III. However, the values of α for the longer members of the bromide series were larger than those reported here, even though their chain lengths were much shorter. For example, the value reported for n-octyl bromide at 25° was 0.226 while that for n-hexadecyl bromide at the same temperature was 0.287. The distribution in the liquid halides was attributed to the existence of the longer molecules in a variety of shapes and to orientation by twisting around the bonds of the molecules, that is, segment orientation, the amount of this twisting increasing with increase in length of the hydrocarbon chain. Since only one molecular shape is possible in the crystal lattice, a distribution suggests a certain amount of segment orientation, as observed in crystalline tripalmitin and tristearin,[11] in which orientation of the molecule as a whole is impossible and the orientation process is accompanied by an abnormally wide distribution of relaxation times. If the orientation in the simple alkyl esters were that of molecular segments alone, one would not only expect a much wider distribution of relaxation times, as observed in the triglycerides, but also no significant increase in relaxation time with the addition of carbon atoms at the end of the chain. The relaxation times listed in Table III show that there is a definite increase at a given temperature with increase in chain length, even though the latter is small compared to the total length of the chain.

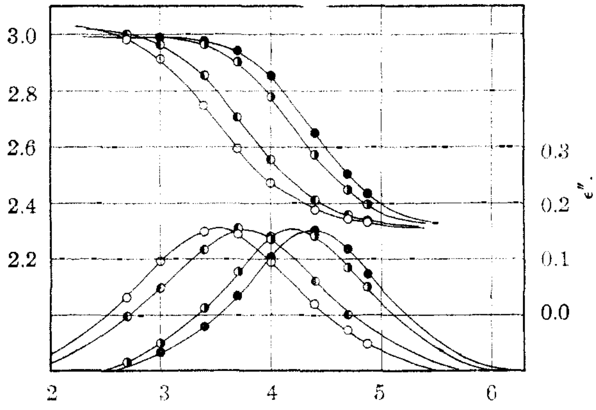

Fig. 7.—The frequency dependence of the dielectric constant and loss factor of n-hexadecyl palmitate at various temperatures: ●, represent data at 19.8°; ◑, at 16.4°; ◐, at 9.0°; ○, at 5.1°.

If dielectric relaxation is treated as a rate process in which the polar molecules orient from one equilibrium position to another,[15,20] the energy $\Delta H^{\ddagger}$ and entropy $\Delta S^{\ddagger}$ of activation may be calculated. The values of the relaxation time, τ, were determined in this investigation by plotting ϵ'' as a function of log f at various temperatures, as shown in Fig. 7 for n-hexadecyl palmitate, and determining the critical frequency, $f_m = 1/2\pi\tau$, by interpolation. The logarithms of τ plotted against $1/T$ for the three esters in Fig. 8 give straight lines. Table III shows that the activation energy increases slightly with increase in chain length. However, there appears to be no definite trend in the values for $\Delta S^{\ddagger}$ with the molecular weight of the ester. This is as it should be if the mechanism is the same in each case. From measurements on long-chain esters in solid solutions of paraffin wax,[22–24] Kauzmann[21] has calculated values for $\Delta H^{\ddagger}$ which are about 2 kcal. lower than those for the pure esters in Table III when allowance is made for difference in chain length. This might be expected, since dilution in a hydrocarbon solvent separates the polar groups, reducing dipole–dipole interaction and thus allowing the chains to orient with greater ease in the lattice. The values of $\Delta S^{\ddagger}$ for the pure esters are slightly higher than those obtained for the solid solutions,[21] but the difference is not enough to be of significance.

Baker and Smyth[4] have reported evidence of restricted orientational freedom in solid ethyl stearate, this freedom persisting down to a sharp monotropic thermal transition at 22.5°. Thermal examinations by Malkin[25] and by Phillips and Mumford[26] have shown that this compound exists in two crystalline forms: α, m.p. 30.4° and β, m.p.

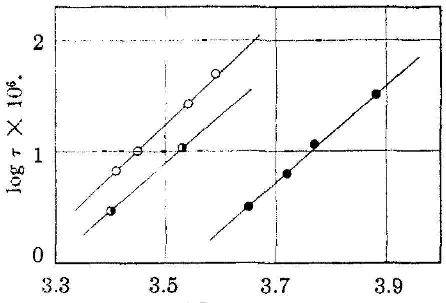

Fig. 8.—The variation of the Briggsian logarithm of the relaxation time with the reciprocal of the absolute temperature for n-hexadecyl palmitate (hollow circles), n-dodecyl stearate (half-filled circles) and n-decyl palmitate (filled circles).

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

[21] W. Kauzmann, *Revs. Modern Phys.*, **14**, 12 (1942).

[22] W. Jackson, *Proc. Roy. Soc.* (*London*), **A150** 197 (1935).

[23] R. W. Sillars, *ibid.*, **A169**, 66 (1938).

[24] D. R. Pelmore, *ibid.*, **A172**, 502 (1939).

[25] T. Malkin, *J. Chem. Soc.*, 2796 (1931).

[26] J. W. C. Phillips and S. A. Mumford, *ibid.*, 1732 (1931).

32.9°. *n*-Octadecyl acetate, an isomer of ethyl stearate in which the polar group is located at the opposite end of the chain, has also been reported to exhibit dimorphism[17,26] with melting points as shown in the third column of Table II. In Fig. 9, the dielectric constant of *n*-octadecyl acetate is plotted as a function of increasing and decreasing temperatures. On cooling, the liquid sample solidified sharply at 30.1° into the transparent α-form with a dielectric constant lower than that of the liquid but high enough to suggest a considerable amount of orientational freedom, probably about the long molecular axis. No frequency dependence of the dielectric constant was observed in this phase. When the sample was cooled below room temperature, small white patches of the stable β-form appeared and grew rapidly throughout the medium. This transformation accounts for the drop in dielectric constant and increase in sample temperature in this region. This phenomenon, however, does not occur at a definite temperature and cannot be compared to the sharp thermal transition found in the α form of ethyl stearate. The transformation can be brought about at any temperature below the β melting point by seeding with the β-form. Once the transformation has taken place, the α form cannot again be isolated until after the sample has been melted and resolidified. The dielectric constant of the rotator phase of this compound is lower than that of the liquid perhaps, because of stronger dipole–dipole interaction in the lattice when the COO group is near the end of the chain. Similar behavior is shown by ethyl stearate.[4]

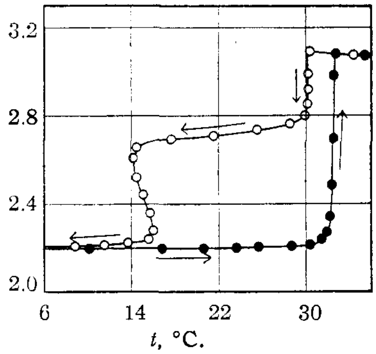

Fig. 9.—The temperature dependence of the dielectric constant of *n*-octadecyl acetate at 5 kc. Hollow circles are for decreasing temperature and filled circles for increasing temperature.

The dielectric behavior of *n*-dodecyl palmitate and *n*-tetradecyl stearate, shown in Fig. 10, indicates that molecular rotation is not possible below their freezing points. The summary in Table III shows that the addition of two methylene groups to the alcohol chain in *n*-decyl palmitate causes rotation to cease, while the further addition of two methylene groups to the acid chain, forming *n*-dodecyl stearate, restores rotational mobility to the molecules. When two more methylene groups are added to the alcohol chain, forming *n*-tetradecyl stearate, a rigid lattice again results. The similarity between *n*-dodecyl palmitate and *n*-tetradecyl stearate is to be expected since the locations of the COO group in the two chains are analogous. The same is true of *n*-decyl palmitate and *n*-dodecyl stearate.

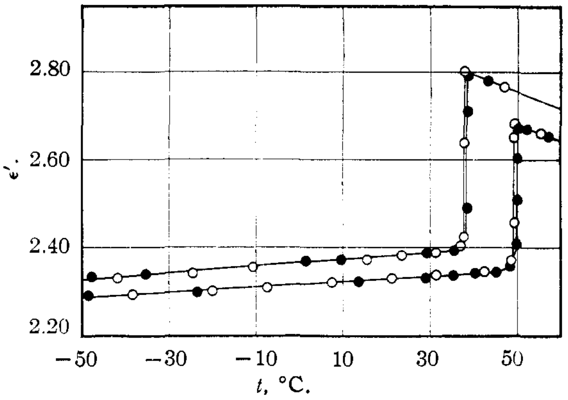

Fig. 10.—The temperature dependence of the dielectric constants of *n*-dodecyl palmitate (upper curve) and *n*-tetradecyl stearate (lower curve). Hollow circles are for cooling and filled circles for warming.

The dielectric constants of solid *n*-dodecyl palmitate and *n*-tetradecyl stearate are significantly higher than can be accounted for by the square of the refractive index even after taking into account the increase in density accompanying solidification. The values tend to decrease gradually with decrease in temperature, although the amount of polarizable material between the condenser plates does not change. An examination of the semicircular arc plots in Figs. 5 and 6 shows that the observed values of ϵ_∞ fall between 2.3 and 2.4, which again is high. Measurements on *n*-hexadecyl palmitate at 19.8 and 5.1° (Fig. 6) show that ϵ_∞ decreases with increase in temperature. Similar behavior was observed for *n*-decyl palmitate and *n*-dodecyl stearate. This excess polarization may be the result of the occasional orientation of a polar molecule or of a librational freedom of the long-chain molecules in the crystal lattice about positions of minimum potential energy without actual passage over the potential barriers preventing rotation. These librations would increase with increase in temperature due to a loosening of the lattice, and, therefore, result in the observed increase in dielectric constant with increase in temperature.

Glycol Esters.—The dielectric constant–temperature curves for ethylene dimyristate, ethylene dipalmitate and ethylene distearate are shown in Fig. 11. Unlike the corresponding triglycerides, these solids showed low dielectric constant, only one melting point, and no transition point. If these molecules extend themselves in single zig-zag chains, it can be seen that their dipole moments would be zero for rotation about the long axis, the moment of one COO group exactly cancelling that of the other in the same molecule. Therefore, no orientation polarization would be realized even if rotation were possible. However, because of the absence of a waxy appearance, common to rotator phases, and the failure to observe any transition point, it is believed that rotational mobility is not present in these solids. The square of the refractive index of ethylene distearate[17] at 75° is 2.07, which is only slightly lower than the dielectric constant found for the solid ester. The increase in density accompanying solidification could easily account for this difference. Very little change in dielectric constant with temperature is evident in these solids.

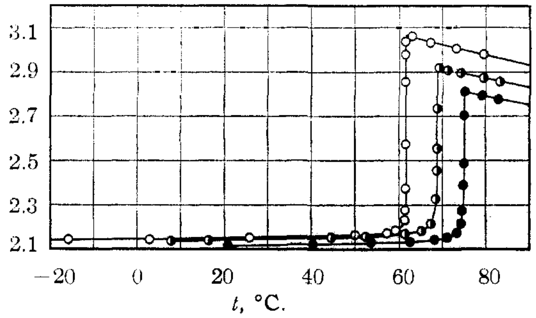

Fig. 11.—The variation of the dielectric constants at 5 kc. of ethylene dimyristate (hollow circles), ethylene dipalmitate (half-filled circles) and ethylene distearate (filled circles) with decreasing temperature.

Stearic Acid.—The dielectric behavior of stearic acid is shown graphically in Fig. 12. Due to the strong tendency of the carboxylic acids to form non-polar dimers in the liquid phase, their dielectric constants are always lower than they would be if only monomers were present. Several investigators have reported that, in the lower acids, the dielectric constant of the liquid increases with increase in temperature due to the thermal dissociation of the dimers,[27,28] resulting in an increase in orientation polarization. With stearic acid, however, the polar group is diluted to such an extent by the long hydrocarbon chain that this effect may be overbalanced by the normal decrease in dielectric constant resulting from decrease in density and increase in thermal agitation of the dipoles. Thus there is a small net decrease in dielectric constant for this compound with increase in temperature even though the total polarization probably increases under these conditions. The sharp peak in the dielectric constant of stearic acid at the freezing point is analogous to those found by Piekara[29] for palmitic acid, stearic acid and oleic acid. The phenomenon may be the result of interfacial polarization between liquid and solid which coexist during the solidification process. As can be seen in Fig. 12, the dielectric constant of solid stearic acid is significantly higher than that of the liquid, probably because of the higher density. Piekara, on the other hand, reports a much lower value for the solid than for the liquid, probably because of the presence of voids. It has been found in this Laboratory that errors due to void formation can be greatly reduced by repeated melting and freezing of the samples before the final measurements are made, since this procedure tends to expel dissolved gases.

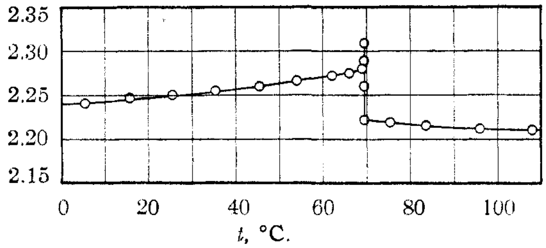

Fig. 12.—The variation of the dielectric constant at 5 kc. of stearic acid with decreasing temperature.

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The Dielectric and Polymorphic Behavior of Cyclohexanol, Cyclohexanone, Chlorocyclohexane and Cyclohexane[1,2]

BY ROBERT W. CROWE[3] AND CHARLES P. SMYTH

The dielectric properties of cyclohexanol, cyclohexanone, chlorocyclohexane and cyclohexane have been investigated over a wide temperature range at frequencies from 0.5 to 100 kilocycles. Cyclohexanol was found to exist in three solid forms instead of two as had previously been reported. In the high temperature form, the molecules possessed freedom of orientation comparable to that observed in the liquid. Both low temperature forms possessed low dielectric constants, indicating an absence of molecular freedom. In the supercooled high temperature form the orientation process involves a small distribution of relaxation times similar to that reported for solid cyclopentanol. Cyclohexanone and chlorocyclohexane were found to exist in two solid forms, with evidence of rotational mobility in their high temperature forms. The rotational transition in chlorocyclohexane was found to be enantiotropic instead of monotropic as had previously been reported. The unusually low value of the dielectric constant of the low temperature form of cyclohexane suggests that the force fields in the crystals increase the binding forces on the electrons so as to decrease the molecular polarizabilities, the effect becoming more pronounced as the density of the solid increases.

It has been known for a number of years that cyclohexane and some of its derivatives are capable of existing in more than one crystalline form. In this respect, they resemble compounds such as *t*-butyl chloride,[4,5,6] *t*-butyl bromide,[4,6] methylchloroform,[7,8] 2,2-dichloropropane,[7] 2-chloro-2-nitropropane[8] and others whose molecules are ap-

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(2) This paper represents a part of the work submitted by Mr. R. W. Crowe 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, 1949–1951.

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