[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Possibility of Molecular Rotation in the Solid Forms of Cetyl Alcohol and Three Long-Chain Ethyl Esters

BY WILLIAM O. BAKER AND CHARLES P. SMYTH

This investigation by the dielectric constant method of the possible rotation of certain long-chain molecules in the solid state[1] was undertaken because X-ray measurements had been interpreted as indicating rotation around the long axes of the molecules of dodecyl alcohol,[2] of certain very long-chain hydrocarbons,[3] and of the alkyl groups in higher alkyl ammonium halides.[4] The existence of transitions in solid ethyl palmitate and ethyl stearate suggested that their molecules might possess freedom of rotation around the long molecular axes in the temperature region just below the melting point. Some freedom of dipole orientation in one solid phase previously had been revealed by dielectric constant measurements upon the complicated ethyl behenate.[5]

The dielectric constants of the polar substances, which are used to decide the question of rotation or non-rotation, were obtained with the same bridge and the general technique described in earlier papers.[6] Temperature–time curves were run with a platinum resistance thermometer. Dissolved gas was removed from the liquids as far as possible by evacuation of the cell in order to reduce the formation of cavities on solidification. The densities of the solids were determined with a stoppered pycnometer of the type used by Richards and Wadsworth,[7] water, in which the substances were found to be insoluble, being used to fill the space left unoccupied on solidification.

Purification.—All four of these high-boiling substances were heated for several hours under a Vigreux fractionating column at low pressures and at temperatures two or three degrees below those at which they would boil under these pressures. The details of purification are given under each substance below and the physical constants which can be used as criteria of purity are included in Table I.

Ethyl Undecylate.—Material from the Eastman Kodak Company was dried over pure phosphorus pentoxide and fractionally distilled three times at reduced pressure.

Ethyl Palmitate.—Material from the Eastman Kodak Company was twice fractionally distilled at reduced pressure, dried over anhydrous copper sulfate and distilled twice again.

Ethyl Stearate.—Material from the Eastman Kodak Company was purified by two fractional crystallizations from ethyl alcohol followed by fractional distillation three times at reduced pressure.

Cetyl Alcohol.—An impure specimen of material was fractionally crystallized twice from benzene and fractionally distilled four times under reduced pressure. The density at 50.0° agrees with the value found by Delcourt[8] for a supposedly very pure sample. The freezing point 47.8° is lower than the value 49.27° given by Meyer and Reid[9] but higher than the value 46.9° given by Landolt–Börnstein. The sample may, therefore, be regarded as of adequate purity.

Experimental Results

The melting, freezing, transition and boiling points together with the values obtained for the densities, the refractive indices for the D sodium line and the molar refractions and polarizations calculated from them are given in Table I. The values of the polarizations of the esters at infinite dilution in heptane at 25° obtained by Mr. George Leoutsacos in this Laboratory are given for comparison.

The dielectric constants ϵ and the specific conductances k (ohm^{-1} cm.$^{-1}$) are given in Table II, for cetyl alcohol, the temperatures being given in the first column and the frequencies in kilocycles across the top of each group of data. As the conductances of the three esters in their final stage of purification were below 10^{-11}, the lower limit of measurement on the bridge, and as their dielectric constants were found to be independent of frequency between 0.5 and 50 kilocycles, the range used, only the dielectric constants at 50 kc. are given in Table II for these substances. Since the material in each case is frozen between the fixed plates of the measuring condenser, the value found for the dielectric constant does not change because of change in the number of molecules per cc. with temperature. Many values of the dielectric constant at intermediate frequencies and temperatures have been omitted for the sake

---

[1] Smyth and Baker, *J. Chem. Phys.*, **5**, 666 (1937).

[2] Bernal, *Z. Krist.*, **83**, 153 (1932).

[3] Müller, *Proc. Roy. Soc.* (London), **A127**, 417 (1930); **A138**, 514 (1932).

[4] Southard, Milner and Hendricks, *J. Chem. Phys.*, **1**, 95 (1933).

[5] Buckingham, *Trans. Faraday Soc.*, **30**, 377 (1934).

[6] Smyth and Hitchcock, THIS JOURNAL, **54**, 4631 (1932); **55**, 1830 (1933).

[7] Richards and Wadsworth, *ibid.*, **38**, 221 (1916).

[8] Delcourt, *Bull. soc. chim. Belg.*, **40**, 284 (1931).

[9] Meyer and Reid, THIS JOURNAL, **55**, 1574 (1933).

TABLE I

VALUES OF PHYSICAL CONSTANTS

	$C_{10}H_{21}COOC_2H_5$	$C_{15}H_{31}COOC_2H_5$	$C_{17}H_{35}COOC_2H_5$	$C_{16}H_{33}OH$
Trans. pt. °C.	....	14.6 17	(22.5)	32.3
M. p., °C.	−22.5	22.5	31.7	
F. p., °C.	−22.5	19.6	30.5	47.8
B. p. (4 mm.), °C.	90–91	155.0–156.0	163–164	155–156(5 mm.)
d(t°C.)	0.8799(0.8°) .8624(25.4°)	0.8825(17.7°) .8577(24.6°)	0.8973(25.0°) .8444(42.0°) .8313(60.1°)	0.8886(25.0°) .8176(50.0°)
n_D(t°C.)	1.42747(25.4°)	1.43842(25.0°)	1.43791(34.1°)	
MR_D	63.8	87.08	95.91	79[10]
P(t°C.)	115.4(0.8°) 113.1(25.4°)	121.2(17.7°) 142.8(24.6°)	123.7(25°) 146.6(42.0°) 140.0(60.1°)	80.2(25°) 143.1(50°)
P_∞(25°C.)	138.1	159.4	168.8	

of brevity, as have also the many preliminary runs on less pure samples.

Discussion of Results

Although n-undecane[11] and undecylic acid[12] show typical α–β crystalline transitions, time-temperature curves with both warming and cooling showed no transition in solid ethyl undecylate. The dielectric constant as shown in Fig. 1 drops sharply on solidification, after which it decreases slowly and uniformly with falling temperature in the manner commonly shown by

TABLE II

DIELECTRIC CONSTANTS AND SPECIFIC CONDUCTANCES

t, °C.	ϵ(50 kc.)	t, °C.	ϵ(50 kc.)	t, °C.	ϵ(50 kc.)
Ethyl Undecylate, Cooling					
28.5	3.48	−22.4	3.87	−22.6	3.31
22.4	3.54	−22.6	3.85	−23.1	3.28
17.0	3.57	−22.7	3.83	−23.2	3.24
8.2	3.65	−23.0	3.78	−23.5	3.13
0.0	3.71	−22.8	3.74	−24.5	3.08
− 9.7	3.80	−22.7	3.68	−29.0	3.03
−18.8	3.87	−22.7	3.57	−34.0	3.01
−20.6	3.89	−22.7	3.47	−38.0	2.96
−21.7	3.90	−22.7	3.39	−42.2	2.93
−22.1	3.88	−22.6	3.35	−47.5	2.90
Ethyl Undecylate, Warming					
−58.8	2.77	−23.1	3.50	−21.5	3.85
−54.9	2.81	−22.7	3.58	−21.2	3.84
−50.5	2.85	−22.5	3.60	−19.9	3.86
−45.3	2.89	−22.4	3.70	−13.8	3.81
−42.3	2.93	−22.3	3.70	−10.3	3.77
−38.0	2.97	−22.2	3.71	− 7.9	3.76
−34.5	3.01	−22.1	3.73	− 1.8	3.70
−30.0	3.08	−21.8	3.77	+ 3.1	3.67
−25.5	3.20	−21.8	3.80	10.4	3.62
−24.9	3.28	−21.8	3.84	18.0	3.58
−24.4	3.34	−21.7	3.87		
−23.5	3.42	−21.6	3.88		
Ethyl Palmitate, Cooling					
39.1	3.12	19.4	3.61	17.5	2.81
33.5	3.16	19.4	3.58	15.3	2.80
28.6	3.18	19.4	3.52	14.6	2.82
22.7	3.19	19.4	3.46	14.3	2.78
22.1	3.20	19.4	3.29	14.1	2.79
21.6	3.20	19.4	3.14	13.6	2.79
21.2	3.20	19.4	3.07	12.1	2.78
20.6	3.20	19.4	2.96	10.8	2.78
20.3	3.21	19.4	2.90	9.2	2.77
19.9	3.21	19.3	2.85	7.7	2.76
19.7	3.42	19.2	2.84	3.8	2.74
19.5	3.54	18.8	2.82		
Warming					
7.4	2.77	17.0	2.76	21.4	3.18
10.0	2.78	18.2	2.80	21.7	3.16
11.7	2.79	19.5	2.81	22.3	3.16
14.7	2.79	20.1	2.86	24.0	3.15
15.3	2.80	20.2	2.94	26.8	3.14
16.1	2.79	20.5	3.05	31.8	3.13
16.7	2.78	20.7	3.11	35.4	3.12
16.9	2.77	21.1	3.17		
Ethyl Stearate, Cooling					
37.1	3.03	30.5	2.78	22.5	2.72
33.9	3.04	30.5	2.73	21.9	2.72
32.0	3.06	29.9	2.73	20.9	2.71
30.8	3.06	28.7	2.75	17.4	2.71
30.6	3.04	27.6	2.75	14.6	2.71
30.5	3.03	25.2	2.76	13.1	2.70
30.5	2.99	23.1	2.77	12.1	2.69
30.5	2.96	22.0	2.76	8.3	2.68
30.5	2.92	22.0	2.75	5.2	2.67
30.5	2.88	22.4	2.74		
30.5	2.85	22.5	2.73		
Warming					
6.3	2.64	27.0	2.66	31.8	2.84
13.5	2.66	29.1	2.66	32.1	2.90
17.2	2.67	29.8	2.64	32.3	2.95
20.3	2.67	30.3	2.65	32.5	2.98
20.7	2.67	30.7	2.67	32.6	3.04
21.9	2.68	30.9	2.69	32.6	3.03
24.3	2.68	31.2	2.72	32.7	3.02
24.9	2.67	31.4	2.75	35.1	3.02
26.0	2.67	31.6	2.80		

---

(10) Müller and Sack, *Physik. Z.*, **31**, 815 (1930).

(11) Huffman, Parks and Barmore, THIS JOURNAL, **53**, 3882 (1931).

(12) Garner and Randall, *J. Chem. Soc.*, **125**, 881 (1924).

TABLE II (*Concluded*)

Cetyl Alcohol, Cooling

Kc	50	5	0.5	50	5	0.5
t, °C.		ϵ			$k \times 10^{10}$	
66.9	3.48	3.48	3.47	..	0.5	0.5
63.7	3.56	3.57	3.59	..	.5	.5
60.7	3.58	3.58	3.59	..	.5	.5
59.0	3.59	3.59	3.59	..	.5	.5
57.8	3.64	3.64	3.60	..	.5	.5
57.3	3.65	3.65	3.62	..	.5	.5
50.9	3.77	3.78	3.77	..	.5	.5
48.3	3.83	3.83	3.81	..	.5	.5
47.8	3.84	3.99	4.09	0.5	20.9	3.6
47.8	3.88	4.36	5.00	11.4	57.0	31.8
47.8	4.08	4.55	6.27	52.0	67.4	53.6
47.8	4.29	4.62	7.15	75.0	68.1	53.3
47.8	4.30	4.66	7.53	75.0	67.6	51.8
47.8	4.31	..	7.75	75.0	..	50.0
43.9	4.30	4.67	7.65	73.5	62.0	40.1
42.7	4.25	4.60	7.59	65.0	57.0	36.8
35.9	4.14	4.43	6.88	45.2	41.1	26.6
35.0	4.13	4.38	6.73	43.5	38.5	24.8
32.3	2.73	2.75	2.93	14.0	3.5	1.0
32.2	2.55	2.63	2.80	14.0	3.2	1.0
30.2	2.45	2.55	2.72	14.0	2.9	1.0
27.4	2.36	2.49	2.63	14.0	2.8	1.0
20.8	2.23	2.31	2.43	12.0	1.9	0.5
15.3	2.16	2.20	2.35	10.6	0.5	.4
4.4	2.12	..	2.28	3.6	..	.4

polar substances in which some of the molecules may have some slight freedom of bending or rotation without the existence of any general rotational freedom. As in the temperature–time curves, no sign is given of any transition. With rising temperature the dielectric constant–temperature curve begins a rapid rise a few degrees below the melting point and does not reach the cooling curve until melting is almost complete. The exact shape of the curve in this immediate region is uncertain as two runs gave a sharp but slight drop when liquefaction was practically completed. The curve in Fig. 1 is roughly rounded off in this region as the two runs did not check very closely. A slight discrepancy between the curves in the liquid region presumably is due to the presence of a few small bubbles of gas between the condenser cylinders. If the temperature reading of the resistance thermometer inside the inner condenser cylinder lagged considerably behind the actual temperature of the material being measured between the cylinders, this apparent rise of the curve before melting would be accounted for, but the fact that the rate of temperature rise in this region was as slow as 1° in twenty minutes eliminates this possible source of error. As the rise of the temperature–time heating curve for the material begins to slacken off just where the dielectric constant curve begins to rise more rapidly and gives no horizontal portion like that in the cooling curve, a difference generally observed between cooling and heating curves, it may be concluded that the structure begins to loosen markedly when the rising temperature reaches this point, possibly because of the melting of small quantities of impurity in the solid. This close agreement between the indications of the dielectric constant curve and the temperature–time curve gives added confirmation of the absence of lag in the temperature readings for the former. The loosening of the structure with an increasing amount of occasional dipole rotation as the region of the melting point is approached has been observed in this Laboratory for many substances[6,13] and recently has been reported for two symmetrical long-chain ketones, $(C_8H_{17})_2CO$ and $(C_{11}H_{23})_2CO$, by Müller,[14] who concludes that, within 15 to 20° of the melting point, an increase of rotational mobility of the chain molecules around the chain axes occurs along with a rapid expansion of the lattice. It seems significant that, in measurements previously published from this Laboratory and in others as yet unpublished, isotropic solids in which the molecules rotate much as in the liquid state have been found to melt sharply with no gradual change but an abrupt break in dielectric constant. Moreover, the samples of the substances showing this behavior were frequently of

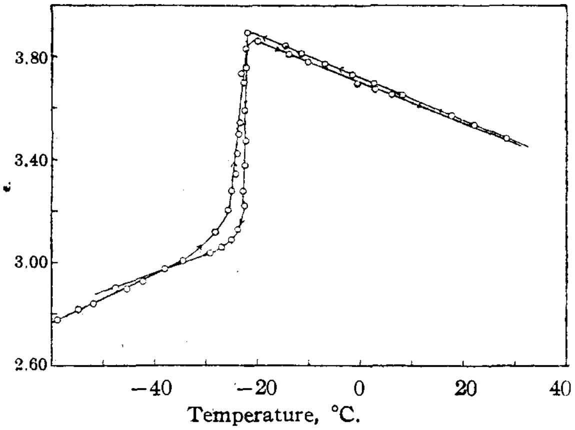

Fig. 1.—Temperature dependence of the dielectric constant (at 50 kc.) of ethyl undecylate. (Arrows indicate the direction in which the temperature is changing.)

---

[13] Smyth and McNeight, THIS JOURNAL, **58**, 1597, 1718, 1723 (1936).

[14] Müller, *Proc. Roy. Soc.* (London), **A158**, 403 (1937).

no greater purity than the materials discussed in this paper.

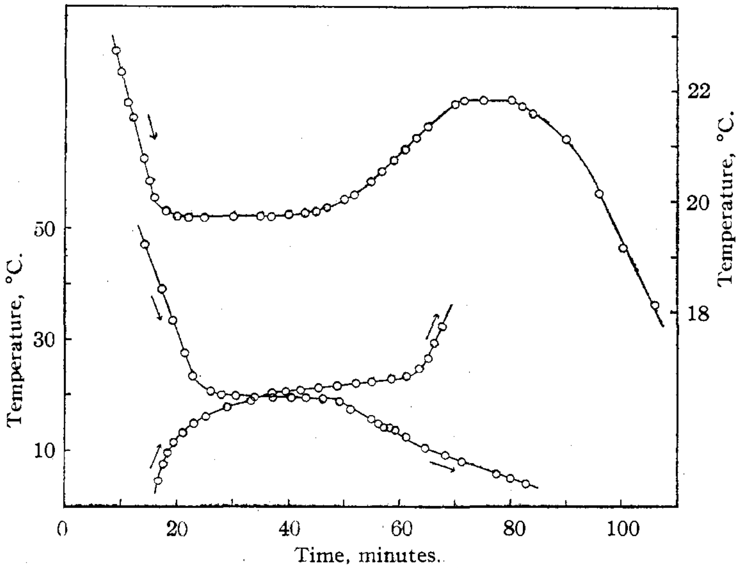

Fig. 2.—Temperature–time curves for ethyl palmitate. Uppermost curve, unpurified sample (temperature scale at right); lower curves, pure sample (temperature scale at left).

A polarizing microscope shows that the solid undecylate is anisotropic throughout the entire temperature region investigated. The failure to find a transition in the solid in spite of those existing in undecane and undecylic acid is understandable since liquefaction of the ester occurs only a few degrees above the melting temperature of undecane and well below the temperature of the transition in undecylic acid, where the formation of double molecules presumably raises the transition and melting temperatures.

The thermal behavior of ethyl palmitate and stearate have been extensively investigated[15–19] and Garner mentions[20] unpublished dielectric constant–temperature curves by Buckingham for methyl and ethyl palmitate and ethyl behenate which show minute sharp peaks at the melting point. The unpurified sample of ethyl palmitate as it came from the manufacturer showed a peculiar temperature–time curve (Fig. 2) like that found by previous investigators. It solidified sharply to a clear crystalline solid, the α-form, which grew opaque as the curve rose rapidly to a second horizontal portion at a temperature 0.7° lower than the melting point of the β-form produced by this transition. After one distillation the material gave the same type of cooling curve although the temperature rise produced by the α–β transition was less sharp. Further purification lowered the freezing point 0.1° from the initial value and eliminated this rise entirely, the α–β transition from clear to opaque occurring without change of temperature on the horizontal portion of the cooling curve. The polarizing microscope showed the clear form first produced to be anisotropic and, therefore, not a glass. Unfortunately, dielectric constant measurements were not made on the impure material which showed the rise in the cooling curve accompanying the α–β transition. A second sample procured later from the same manufacturer failed to show the rise, while addition of ethyl stearate, a suspected impurity, to a well purified sample did not restore the rise in the curve. A very slight halt appears on the cooling curve at 14°, indicating a hitherto unreported transition, which is confirmed by the nick at 14.6° in the dielectric constant curve for falling temperature and at 17° in the curve for rising temperature (Fig. 3). The temperature–time curve for rising temperature is similar in form

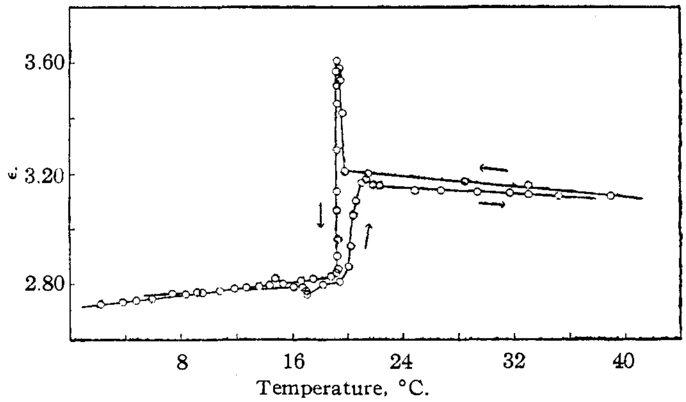

Fig. 3.—Temperature dependence of the dielectric constant (at 50 kc.) of ethyl palmitate. (Arrows indicate the direction in which the temperature is changing.)

---

[15] Smith, *J. Chem. Soc.*, 802 (1931).

[16] Phillips and Mumford, *ibid.*, 1732 (1931); 898 (1932).

[17] Malkin, *ibid.*, 2796 (1931).

[18] King and Garner, *ibid.*, 1449 (1934).

[19] Francis, Collins and Piper, *Proc. Roy. Soc.* (London), **A158**, 691 (1937).

[20] Garner, *Trans. Faraday Soc.*, **30**, 775 (1934).

to that for ethyl undecylate. The melting point 22.5° is the temperature at which the solid β-form and the liquid are in equilibrium.

The dielectric constant of ethyl palmitate throughout the temperature range investigated is independent of frequency between 0.5 and 50 kilocycles, while the specific conductance is below the lower limit 10^{-11} attainable with the bridge. A very small peak in the curve at the melting or freezing point like that in the rising temperature curve in Fig. 3 has been reported for a number of substances[21] and may be attributable to a slight Maxwell–Wagner effect resulting from the coexistence of the liquid and solid phases or, possibly, to the existence between the condenser cylinders of an abnormal number of molecules during the establishment of equilibrium. The large peaks previously observed in a very few cases[22,23] have been accompanied by increased conductance and anomalous dispersion. Although such a peak in the acetic acid curves has been cited as evidence of the formation of molecular aggregates or swarms in the liquid as the freezing point was closely approached, they may be interpreted as due to Maxwell–Wagner effects, that is, absorption of electrical energy and apparent increase in dielectric constant resulting from the coexistence over a small range of temperature, due to impurities, of finely dispersed liquid and solid phases of different dielectric constants and different and not inconsiderable conductances. The curves for ethyl palmitate were run repeatedly with different rates of cooling. Approximately the same peak was obtained each time, although it was widened when the rate of cooling was too great to permit of temperature equilibrium. The high sharp peak appears to be unique in that it is unaccompanied by anomalous dispersion and cannot be attributed to a Maxwell–Wagner effect. As the peak occurs only on the cooling curve and apparently develops when the α–β transition is going on, it may be attributed to the development of molecular freedom caused by a molecular disorder greater during the process of transition than that existing in the liquid state where the molecules are more or less oriented. In other words, the potential hump to be crossed by a molecule in order to rotate is lower on the average during the transition in the solid than it is in the liquid state. The polarization of the β-form at 17.7° is 34.1 higher than the molar refraction of the liquid and only 21.6 lower than the polarization of the liquid at 24.6°, indicating that a not inconsiderable freedom of dipole orientation still exists in the solid near the melting point. The slow decrease of dielectric constant with falling temperature is interrupted by a slight but reproducible hump at 14.6° caused by the transition previously mentioned in connection with the temperature–time cooling curve. With rising temperature the transition makes itself apparent in the slight depression at 17°. The rising temperature curve starts upward sharply at the temperature of the freezing point and reaches a maximum just below the melting point. The minute hump or maximum is so small as to be of doubtful significance. The situation may be complicated by the presence of small cavities in the solid, which make themselves evident as the presumable cause through gas bubble formation of the slight difference between the two dielectric constant curves for the liquid. One is tempted to suggest that these soft solids may rapidly loosen their structures two or three degrees below the temperature of actual liquefaction. The dielectric constants of many other solids have indicated the possibility of some slight dipole orientation even when no general rotational freedom was found. As an unusually great possibility of such orientation is indicated by the large excess of the polarization values for these solids over the molar refraction values, an exceptional loosening of the structure would not be strange. The phenomenon might be attributable to the presence of liquid in the solid below the melting point because of the presence of impurities, but, in the absence of a Maxwell–Wagner effect, it would seem that the amount of liquid necessary to give the rise would be much greater than that which could exist in these samples.

The sample of ethyl stearate in its earlier stages of purification showed a very high conductance which disappeared in the later stages. The temperature–time curves (Fig. 4) are typical of a substance showing a monotropic transition. The cooling curve gives freezing and transition temperatures in close agreement with those given by the dielectric constant–temperature curve (Fig. 5) obtained with falling temperature, both showing a temperature rise of about 0.6° when the α–β transition occurs and the material changes

---

(21) Piekara, *Physik, Z.*, **37**, 624 (1936).

(22) Errera, *Trans. Faraday Soc.*, **24**, 162 (1928); *Physik. Z.*, **29**, 426 (1928).

(23) Yager and Morgan, THIS JOURNAL, **57**, 2071 (1935).

from transparency to opacity. The slight linear rise of the dielectric constant curve from the freezing to the transition point indicates a restricted freedom of molecular rotation, presumably around the long axis of the molecule, the polarization at 25° being approximately midway between that of the liquid just above the freezing point and the molar refraction. Below the transition the curve resembles closely that for the β-form of ethyl palmitate and may be interpreted similarly. The rising temperature curve, although showing no transition, begins to decrease at a point near the transition temperature on the cooling curve and parallels the cooling curve in the same region. This decrease with rising temperature suggests that the increasing freedom of dipole orientation with rising temperature actually becomes so great that the increase of thermal agitation may more than compensate for the increase in freedom with further temperature rise. The apparently gradual melting has been discussed in connection with the palmitate.

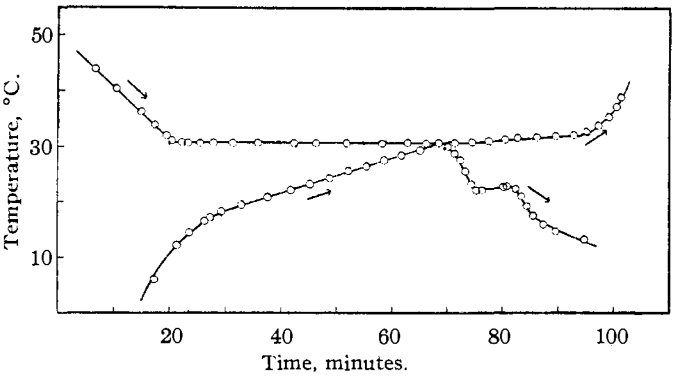

Fig. 4.—Temperature–time curves for ethyl stearate. (Arrows indicate the direction in which the temperature is changing.)

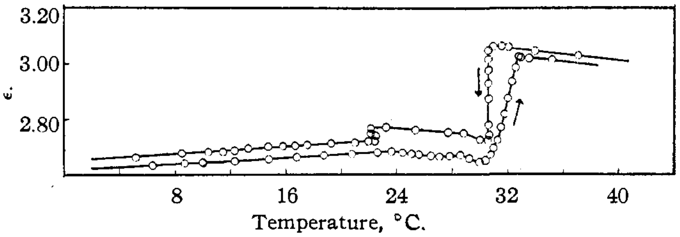

Fig. 5.—Temperature dependence of the dielectric constant (at 50 kc.) of ethyl stearate. (Arrows indicate the direction in which the temperature is changing.)

Both the temperature–time and the dielectric constant–temperature curves for ethyl stearate with falling temperature gave a definite reproducible temperature 22.5° for the α–β transition, which seemed to occur at a normal rate, but other investigators have reported 25.5–26.0°[17] and 27°.[18] To examine the question further, 20 g. of the stearate was melted and allowed to solidify around the bulb of a thermometer in a long thin-walled glass tube, which was deeply immersed in a thermostat set at 25.8°. After twenty-three hours at this temperature, the initially clear α-form had changed to an opaque form, which gave no halt on a temperature–time curve obtained by cooling after removal from the bath. In other words, the α–β transition had occurred at 25.8°, but several hours had been required for it to do so. The experiment was repeated with the thermostat set at 29.3°. After twelve hours the stearate had developed some opacity but less than before. The material now gave a cooling curve with a halt at 23.9°, but with a smaller heat emission than that occurring when the transition was originally observed at 22.5°. The true transition temperature must therefore be regarded as uncertain.

Cetyl alcohol resembles ethyl palmitate in that its dielectric constant rises sharply on solidification (Fig. 6), but differs in that no sharp peak occurs and in that the height of the rise depends upon the frequency used in the measurement, strong anomalous dispersion occurring throughout the

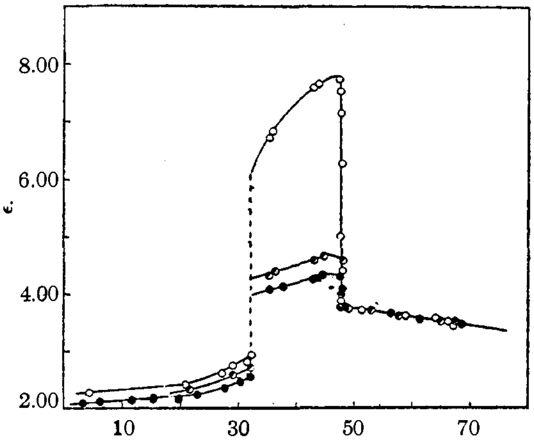

Fig. 6.—Temperature dependence of the dielectric constant of cetyl alcohol with falling temperature. (Hollow circles represent values at 0.5 kc., half filled circles values at 5 kc., and filled circles values at 50 kc.)

region between the freezing point and an α–β transition at 32.3°, at which temperature the temperature–time curve (Fig. 7) shows a halt. Below this transition, a slight anomalous dispersion occurs, but, within 15° of it, the dielectric constant has fallen to values so low that the amount of dipole orientation occurring must be almost negligible. The α-form existing between the freezing and the transition point shows the dielectric behavior of a viscous liquid. That this is not the effect of impurities giving rise to a Maxwell–Wagner effect is shown by the length of the temperature region over which the phenomenon exists, by the sharpness of the boundaries of this region and by the absence of appreciable conductance in the liquid. The values in Fig. 8 of the imaginary part of the dielectric constant, $\epsilon'' = 1.8 \times 10^{12}\ k/f$, where f is the frequency in cycles and k the specific conductance, are a maximum at the freezing point just as solidification is complete, the symmetry normally occurring in such curves being prevented by the proximity of the maxima to the freezing point. It may be concluded that the molecules in the α-form have a freedom of rotation, which, like that of a viscous liquid, decreases with falling temperature. This conclusion is consistent with the lower density found for the α-form as compared to the β-[24] and the much lower entropy of fusion 22.1 calculated for cetyl alcohol from its heat of fusion[25] as compared to those of hexadecane 39.2 and heptadecane 41.3,[26] the molecules of which are not rotating in the solid. The hydrocarbons and the alcohol should have approximately the same entropies of fusion if the latter did not possess rotational freedom in the solid state.

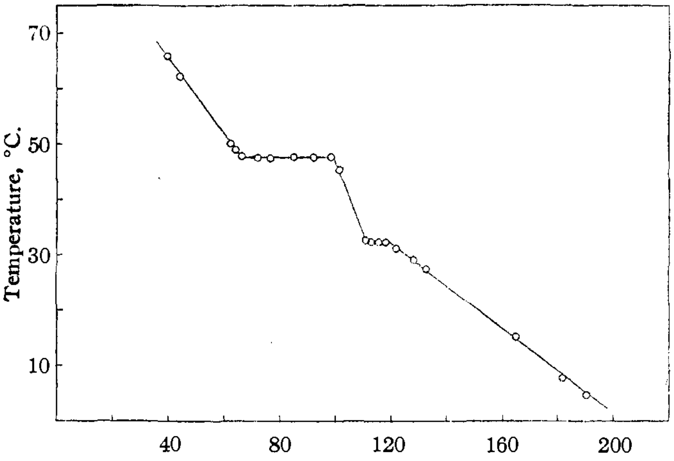

Fig. 7.—Temperature–time curve (cooling) for cetyl alcohol.

After the completion of these measurements values were published by Higasi and Kubo[27] which are difficult to reconcile with these results for cetyl alcohol. Their determinations carried out only at 3000 kc. give a maximum at 35°, the values being intermediate between those at 5 and at 0.5 kc. in Fig. 6, while one would, of course, expect them to be lower than those at 50 kc. As the purity of their material is not given and as they obtain no precise indication of the α–β transition, of which they seem to be unaware, it appears unwise to discuss their results.

X-Ray investigations[17,19,28,29] have shown that the long rod-like molecules of ethyl stearate, cetyl alcohol and other long-chain compounds have their ends in parallel planes and their long axes perpendicular to these planes in the α-forms and inclined at an angle to the planes in the β-forms. The latter is also true of the β-form of ethyl palmitate. The α-form of the esters has a larger transverse cross-sectional area per molecule,[29–31] and a larger specific heat than the β-form.[18]

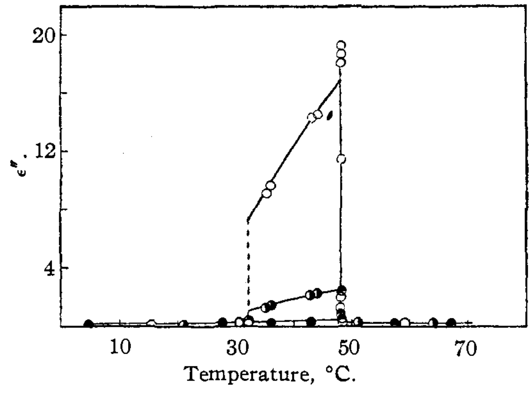

Fig. 8.—Temperature dependence of the imaginary part ϵ'' of the dielectric constant of cetyl alcohol with falling temperature. (Hollow circles represent values at 0.5 kc., half filled circles values at 5 kc., and filled circles values at 50 kc.)

---

[24] Deffet, *Bull. soc. chim. Belg.*, **44**, 97 (1935).

[25] Landolt-Börnstein (5th ed.).

[26] Parks and Todd, *Ind. Eng. Chem.*, **21**, 1235 (1929).

[27] Higasi and Kubo, *Bull. Chem. Soc. Japan*, **12**, 326 (1937).

[28] Malkin, THIS JOURNAL, **52**, 3739 (1930).

[29] Wilson and Ott, *J. Chem. Phys.*, **2**, 231 (1934).

[30] Müller and Saville, *J. Chem. Soc.*, **127**, 599 (1925).

[31] Müller, *Helv. Phys. Acta*, **9**, 626 (1936).

Bernal[2] concluded from X-ray data that the dodecyl alcohol molecule rotated around its long axis in the solid just below the melting point and not at lower temperatures. In agreement with the indications of the dielectric constant data, these facts indicate that, when the long axes of the molecules lie perpendicular to the planes in which their heads lie, they may rotate around their long axes, thereby permitting their dipoles to make some contribution to the dielectric constant and raise its value above that of a similar solid in which no molecular rotation is possible. This does not preclude the possibility of some slight intramolecular dipole orientation through turning of groups in the molecule as found by Bridgman and Williams[32] nor does it mean the complete absence of the orientation of an occasional molecule in the β-lattice. It does mean, however, that the major part of any excess of the polarization of these solids over that arising from mere electronic shifts is due to molecular rotation, and by molecular rotation is meant not necessarily completely free rotation about the long axis of the molecule but also an ability to rotate from one position of minimum potential energy in the lattice to another.

Summary

The dielectric constants of ethyl undecylate, palmitate and stearate and cetyl alcohol have been measured over a wide range of temperature and frequency in the liquid and solid states in order to investigate the possibility of molecular rotation in the solid forms. Ethyl undecylate shows no general freedom of molecular rotation in the solid, the melting temperature evidently being too low to permit the molecules to acquire sufficient rotational energy to overcome the intermolecular forces. Ethyl palmitate undergoes a solid α–β transition at its freezing point and, during the process, shows greater freedom of molecular rotation than in the liquid. It also shows a slight transition in the β-form not hitherto detected. Ethyl stearate shows molecular rotation around the long axis in the α-form. Cetyl alcohol shows molecular rotation in the α-form accompanied by strong anomalous dispersion of the dielectric constant. In the α-forms where the long molecules lie perpendicular to the planes in which their heads lie, rotation around the long axes of the molecules appears to be possible, but, in the β-forms where the molecules are tilted with respect to the planes and more closely packed, no general freedom of rotation is found.

PRINCETON, NEW JERSEY RECEIVED MARCH 7, 1938

---

(32) Bridgman and Williams, THIS JOURNAL, **59**, 1579 (1937).

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE, COLLEGE OF CITY OF NEW YORK]

Alkanolamines. V. Reaction of *m*-Dinitrobenzene with Ethanolamines

BY M. MELTSNER, I. KIRSHENBAUM AND A. STEMPEL

Clark[1] reported that 2,4-dinitrochlorobenzene reacted with monoethanolamine to yield 2,4-dinitrophenylaminoethanol.

Raccui[2] found that 3,4,6-trinitrotoluene condensed with di- and triethanolamines to give addition compounds.

Inasmuch as no reduction products were reported, contrary to our experience with nitrobenzene and nitrochlorobenzene, as described in previous papers,[3] we thought it advisable to publish our results with *m*-dinitrobenzene and the ethanolamines.

3,3′-Dinitroazoxybenzene, 3,3′-diaminoazoxybenzene, 3,3′-diaminoazobenzene and an addition product containing 2 moles of 3,3′-diaminoazoxybenzene and 3 moles of triethanolamine were isolated as products of the reaction between the dinitro compound and the three ethanolamines. Traces of nitroaniline were found but no phenylenediamine. As each of the ethanolamines shows a different alkalinity, the yields of each product would vary with the type and concentration of each ethanolamine. Since previous experiments have shown that azo compounds can be reduced by ethanolamines to amines, the non-formation of phenylenediamine is probably due to decomposition at the temperature of the experiments. The formation of an addition product of the diaminoazoxybenzene would seem to indicate that addition precedes reduction.

Experimental

Reduction with Diethanolamine and Water.—Eighty-four grams of diethanolamine and 20 cc. of water were added

---

(1) Clark, *Ind. Eng. Chem.*, **25**, 1385 (1933).

(2) Raccui, *C. A.*, **29**, 6217 (1935).

(3) Meltsner, *et al.*, THIS JOURNAL, **59**, 2660 (1937); Kremer, *ibid.*, **59**, 1681 (1937); Kremer and Kress, *ibid.*, **60**, 1031 (1938).