hence ΔH for the dissociation is 27,600 calories within the indicated temperature range.

Results of the addition of hydrogen selenide to ammonia at 21°, Table IV, show that the two gases react mole for mole in the formation of the white crystalline solid. Therefore, the product must be NH_4HSe.

TABLE IV

Ml. of $H_2Se + H_2$	Ml. of H_2Se	Ml. of NH_3 required
26.6	25.0	25.0
23.4	21.9	22.2
27.7	25.9	25.8
22.4	20.9	21.1

Summary

1. The equilibrium for the dissociation of ammonia hydroselenide, $NH_4HSe(s) \rightleftarrows NH_3(g) + H_2Se(g)$, was determined in the temperature range 15° to 30.1°.

2. ΔH for this reaction was found to be 27,600 calories in the indicated temperature range.

HOUGHTON, MICHIGAN RECEIVED SEPTEMBER 28, 1948

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Molecular Rotation in the Solid Forms of Some Long-Chain Alcohols[1]

BY JOHN D. HOFFMAN AND CHARLES P. SMYTH

X-Ray investigations on *n*-dodecyl alcohol conducted by Bernal[1a] resulted in the conclusion that the molecules rotate about their long axes several degrees below the freezing point. This result is not in accord with the more recent X-ray measurements of Ott[2] who found no evidence for rotation. Dielectric data on this substance obtained by Frosch[3] at audio frequencies disclosed strong frequency dispersion below the freezing point which would require molecular rotation in the solid if interpreted in the usual way, but the results showed great complexity and were not reproducible.

Dielectric measurements[4] on *n*-hexadecyl alcohol carried out at 0.5, 5.0 and 50 kc. indicated molecular rotation in a definite temperature range below the freezing point. It is noted that the dielectric loss factor, ϵ'', in this range, which we term the "waxy" range to avoid the term "glassy," greatly exceeded the theoretical limit for orientation loss imposed on it by the relation $\epsilon''_{\max} = (\epsilon_0 - \epsilon_\infty)/2$. Furthermore, the dielectric constant ϵ' rose sharply on freezing and was frequency dependent. The rise in dielectric constant would seem to demand greater molecular freedom in the solid than in the liquid, which is contrary to the fact that entropy must decrease on freezing. It must be pointed out, however, that X-ray observations[2] on *n*-hexadecyl alcohol showed that hexagonal close-packing of the molecular chains persisted for some degrees below the freezing point, which strongly suggests molecular rotation in the solid. Frosch explained the high value of the dielectric constant mentioned above as due to the co-existence of liquid and solid phases between the condenser plates, which resulted in Maxwell–Wagner polarization. The persistence of the liquid phase in contact with the solid for a long period of time at a temperature several degrees below the freezing point appears highly improbable, although a treatment based on this model accounted quantitatively for the observed dielectric constants.

The present work undertakes the study of the reported transition in *n*-dodecyl alcohol, and the investigation of the dielectric and thermal behavior of *n*-tetradecyl, *n*-octadecyl and *n*-docosyl alcohols with emphasis on the status of molecular rotation about the long axis and the isolation of the factors leading to time and frequency dependence of the abnormally high dielectric constants.

Experimental Method

The bridge employed for the measurements was essentially that described in previous papers.[5] The frequency range and stability of the equipment were improved by using a Hewlett-Packard 200 oscillator as a signal generator and a TS12/AP amplifier (Presto Recording Corp.) as a null detector. Teflon spacers were inserted between the gold cylinders of the dielectric cell (C_0 = 38.6 $\mu\mu$f.; liquid capacity, 8 cc.) instead of the customary mica tabs with the result that loss across the tabs was eliminated. All temperature measurements were made with a calibrated platinum resistance thermometer.

The dielectric constants were determined by calculating the ratio, $\epsilon' = C/C_0$, where C is the capacitance of the cell containing the material, exclusive of lead and insulator capacitance, and C_0 is the corresponding vacuum capacitance. The specific conductivity in ohms^{-1} cm.$^{-1}$ was calculated from the relation $k = 0.0885/RC_0$ where R is the resistance of the cell in ohms as measured in the bridge, C_0 being expressed in $\mu\mu$f. ϵ'' was calculated from k by using the relation $\epsilon'' = 1.8 \times 10^{12}\ k/f$, where f is the frequency of the measurements in cycles/sec. The error in ϵ' never exceeds ±1%, and the reproducibility in the ϵ'' measurements is better than ±3% except for very low values where the error becomes greater.

Purification of Materials

n-Dodecyl alcohol ($C_{12}H_{25}OH$) was purified by crystallization from dry ether followed by five fractional distillations at 1 mm., f.p. 23.5°. Beilstein (I-432) gives the f.p. as 24°.

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[1] This research was carried out with the support of the Office of Naval Research.

[1a] Bernal, *Nature*, **129**, 870 (1932).

[2] Ott, *Z. physik. Chem.*, **193**, 218 (1944).

[3] Frosch, *Ann. Physik*, **42**, 254 (1942).

[4] Baker and Smyth, THIS JOURNAL, **60**, 122 (1938).

[5] Smyth and Hitchcock, *ibid.*, **54**, 4631 (1932); *ibid.*, **55**, 1830 (1935).

n-Tetradecyl alcohol ($C_{14}H_{29}OH$) was dried over calcium oxide and fractionally distilled twice at 1 mm. pressure; f.p. 36.4°, transition point 34.4°. Phillips and Mumford[6] list 37.7° and 35° for these points, respectively. Trapeznikov[7] gives the m.p. of the anhydrous crystals as 36.7° and of the hydrate as 40°.

n-Octadecyl alcohol ($C_{18}H_{37}OH$) was purified by crystallization from dry ether twice and benzine twice, and was distilled three times at 1 mm. pressure; f.p. 57.7°, transition point 53.4°. Phillips and Mumford[6] list 57.95° and 53.8° for these points, respectively. According to Trapeznikov[7] the melting point of the anhydrous crystals is 58.4°, and that of the hydrate 61.5°.

n-Docosyl alcohol ($C_{22}H_{45}OH$) synthesized by Mr. E. N. Stirewalt was kindly given us by Dr. Nathan L. Drake of the University of Maryland. This sample was subjected to a single high vacuum distillation (about 10^{-2} mm.) after drying for two weeks in a vacuum desiccator, f.p. 69.6°, transition point 64.5°. Francis, Collins and Piper[8] list the f.p. as 70.8°. The transition point has not been reported previously.

In all cases, the transfer of alcohols was performed under dry conditions and every effort was made to avoid contamination with water or ionic impurities. The cooling curves and low specific conductivities of the liquids indicate the purity of these compounds.

Experimental Results

The dielectric constants, ϵ', the specific conductivities, k, and the loss factors, ϵ'', obtained on cooling and on subsequent re-heating of each of the compounds are given in Table I. Many values of a confirmatory nature have been omitted, and only portions of the data near transitions are included. The data in Table I are plotted in Figs. 1, 2, 3 and 4. *n*-Octadecyl alcohol was also measured on a heterodyne beat apparatus[9] at a frequency of 525 kc. in the same dielectric cell used in the impedance bridge. The data are plotted in Fig. 3 (filled squares) but are not reproduced in Table I because of their closeness to the values at 50 kc. Arrows in the diagrams indicate the direction in which the temperature is changing. Figures 5 and 6 show the behavior of the dielectric constant at 0.25 kc. for *n*-tetradecyl and *n*-octadecyl alcohols, where the normal cooling process was intentionally halted for several hours in the waxy state by holding the temperature of the

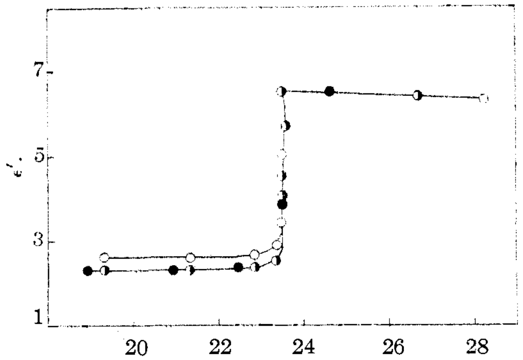

Fig. 1.—Temperature dependence of the dielectric constant of *n*-dodecyl alcohol. Hollow circles represent values at 0.5 kc., half filled circles values at 5.0 kc., and filled circles values at 50 kc.

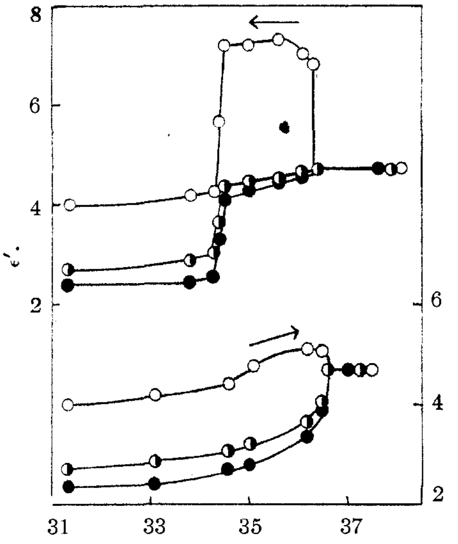

Fig. 2.—Temperature dependence of the dielectric constant of *n*-tetradecyl alcohol. Hollow circles represent values at 0.5 kc., half-filled circles values at 5.0 kc., and filled circles values at 50 kc. Upper curve scale on left, lower curve scale on right. Arrows indicate direction in which temperature is changing.

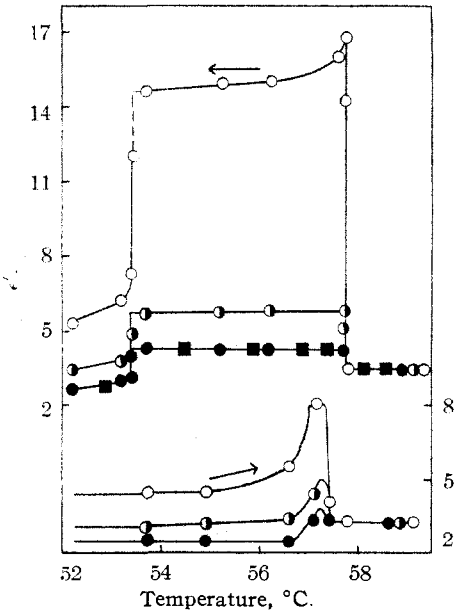

Fig. 3.—Temperature dependence of the dielectric constant of *n*-octadecyl alcohol. Hollow circles represent values at 0.5 kc., half-filled circles values at 5.0 kc., filled circles values at 50 kc., and filled squares values at 525 kc. Upper curve has scale on left, lower curve scale on right. Arrows indicate direction in which temperature is changing.

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[6] Phillips and Mumford, *J. Chem. Soc.*, 235 (1933).

[7] Trapeznikov, *Acta Physicochem., U. R. S. S.*, **XX**, 589 (1945).

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

[9] Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

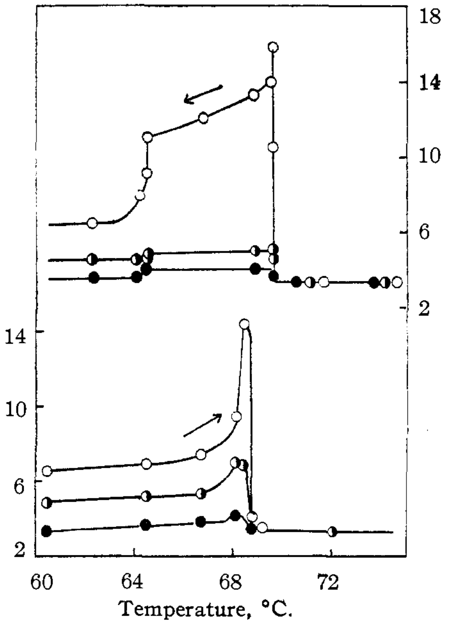

Fig. 4.—Temperature dependence of the dielectric constant of *n*-docosyl alcohol. Hollow circles represent values at 0.5 kc., half-filled circles values at 5.0 kc., and filled circles values at 50 kc. Upper curve has scale on right, lower curve scale on left. Arrows indicate direction in which temperature is changing.

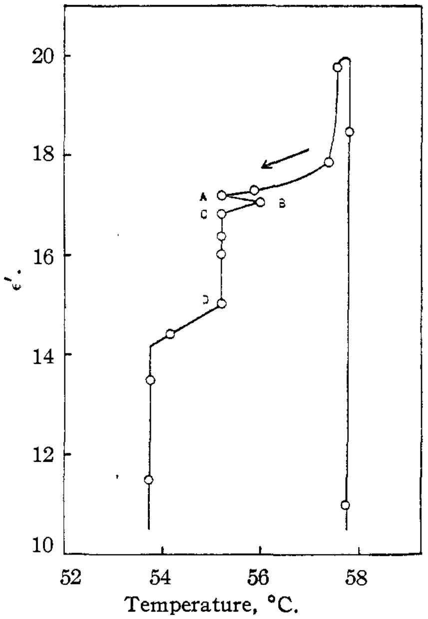

Fig. 6.—Temperature dependence of dielectric constant of *n*-octadecyl alcohol at 0.25 kc. The sample was cooled in the usual way to 55.2° (A), warmed to 56.0° (B). cooled to 55.2° (C) and held at constant temperature for six and one-half hours. The dielectric constant fell to (D). Normal cooling was then allowed to resume.

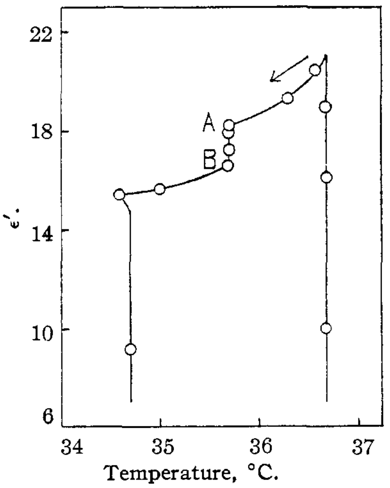

Fig. 5.—Temperature dependence of dielectric constant of *n*-tetradecyl alcohol at 0.25 kc. The sample was cooled in the usual way to 35.7° where it was held for one hour. The dielectric constant dropped from A to B. Normal cooling was then allowed to resume.

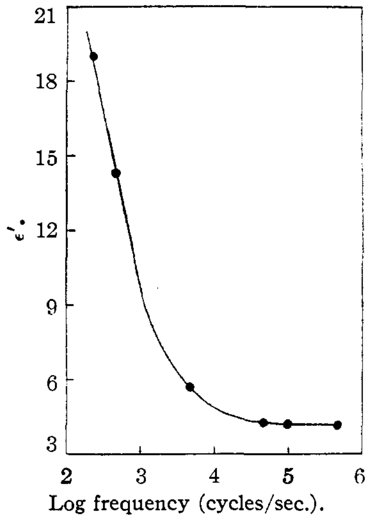

Fig. 7.—Dependence of dielectric constant on frequency for *n*-octadecyl alcohol in waxy state. Data are average values obtained from several runs at 57°.

surroundings constant. After a suitable interval, the normal cooling process was allowed to proceed. Only the upper parts of the curves are shown since the other portions are repetitions of Figs. 2 and 3. In *n*-octadecyl alcohol the points ABCD were measured consecutively in order to check the reversibility of the changes taking place. A typical example of the dependence upon frequency of the dielectric constant of *n*-octadecyl alcohol in the waxy state is shown in Fig. 7. The decrease of ϵ' at 0.25 kc. with time for solid *n*-octadecyl alcohol which had been rapidly cooled from 100 to 15° and held at that temperature for one hundred and fifteen hours is shown in Fig. 8. Figure 9 gives the maximum value of ϵ' at 0.5 kc. attained by this alcohol on freezing as a function of the logarithm of the

TABLE I

DIELECTRIC CONSTANTS AND SPECIFIC CONDUCTIVITIES

n-Dodecyl Alcohol

T, °C.	ϵ'			ϵ''			$k \times 10^{10}$		
	0.5	5.0	50 kc.	0.5	5	50 kc.	0.5	5	50 kc.
(Cooling)									
32.1	..	6.07	..	...	0.58	..		16	..
28.2	6.32	..	..			0.06		..	15
26.7	..	6.36	..		.61			17	
24.6	..	..	6.52					..	
23.5	..	6.55			.61			17	
23.6	6.02	5.68	5.60		.50			14	
23.5	5.02	4.57	4.48		.32	.03		8.9	9
23.5	4.03	4.00	3.90		.25			6.9	
23.4	3.42	3.00	2.92		.13			3.7	
23.3	2.80	2.52	2.55		.09	.00		2.5	0
23.2	2.72	2.42	2.42		.09			2.5	0
22.8	2.62	2.40	2.40		.09			2.5	0
21.3	2.55	2.33	2.33		.07			2.0	0
19.3	2.52	2.31	2.31		..			..	0
15.3	2.43	2.28	2.28		.03			0.7	0
− 1.6	..	2.27	..						
−128	..	2.20	..						
−170		2.18							
(Warming)									
20.8	2.60	2.32	2.32		.03			.7	
21.3	2.75	2.48	2.48		.09			2.5	
23.2	3.40	2.90	3.02		..			..	
23.5	4.00	3.40	3.28		.26			7.3	
23.6	5.12	4.92	5.10		.40			11	
23.7	6.40	6.40	6.40		.65			18	
24.0	6.38	6.38	6.38		.65			18	
25.2	..	..	6.30		..			..	
n-Tetradecyl Alcohol (Cooling)									
48.2	4.42	4.41	4.40	2.5	0.25	0.03	6.9	6.4	6.9
38.1	4.72	4.72	4.72	2.6	.25	.03	7.2	6.9	6.9
36.4	4.82	4.81	4.72[b]	3.4	..	..	9.6	..	..
36.3	6.80	4.70	4.60	7.9	.79	1.4	22[b]	22[b]	40
36.1	7.02	4.65	4.55	7.9	1.0	..	22	28	..
35.6	7.30	4.52	4.48	7.2	1.0	..	20	28	..
35.0	7.20	4.45	4.25	6.1	1.1	..	17	29	..
34.5	7.18	4.35	4.12	6.1	..	..	17	..	..
34.4	5.65	3.60	3.28	2.7	..	..	7.6	..	..
34.3	4.28	3.03	2.56	1.4	.60	..	4.0	18	..
33.8	4.20	2.85	2.45	1.4	.61	..	4.0[b]	17[b]	..
31.1	4.00	2.73	2.40	1.3	.54	..	3.4	15	..
24.7	3.40	2.48	2.25	1.2	.40	0.0	3.3	11	22
(Warming, after remaining at 20° one hour)									
33.1	4.18	2.85	2.40	1.1	.36	.09	3.3	10	26
34.6	4.40	3.05	2.70	1.8	.65	..	5.0	18	..
35.1	4.78	3.20	2.80	2.4	.68	..	6.8	19	..
36.2	5.10	3.65	3.35	3.1	.72	.14	8.5	20	40
36.5	5.05	4.05	3.88	3.1	.58	..	8.5	16	..
36.6	4.80	4.38	4.36	2.7	.58	..	7.5	16	..
36.6	4.72	4.58	4.58	2.7	.40	..	7.5	11	..
37.0	4.68	4.68	4.67	2.5	.23	..	7.0	6.5	..
37.7	4.62	4.62	4.62	2.5	.23	.03	7.0	6.5	6.5
(Separate run, cooling)									
13		2.23							
− 40		2.19							
−105		2.17							

TABLE I (*Concluded*)

T, °C.	ε′			ε″			$k \times 10^{10}$		
	0.5	5.0	50 kc.	0.5	5	50 kc.	0.5	5	50 kc.
n-Octadecyl Alcohol (Cooling)									
63.3	3.35	3.35	3.35	0.00	0.00	0.00	0.04	0.04	0.04
58.8	3.41	3.41	3.41						
57.8	3.42	3.42	3.42[b]						
57.7	3.62	3.65	3.50	7.2	.79	.12	20	22	32
57.7	14.3	5.08	4.05	23	4.7	.54	65	130	150
57.7	16.8	5.78	4.25	27	5.2	.68	75[b]	145[b]	190[b]
57.6	16.0	5.80	4.24	21	5.2	.57	62	145	160
56.2	15.0	5.76	4.22	19	4.3	.57	53	120	160
55.2	14.9	5.72	4.21	19	4.2	.54	52	117	150
53.7	14.6	5.65	4.21	16	3.9	.52	45	108	145
52.9	13.3	4.88	4.11	13	..	..	36	..	..
53.4	11.9	4.35	3.80	10	2.6	.30	28	73	84
53.4	7.35	3.90	3.10	3.6	1.0	.30	10	28	85
53.2	6.08	3.70	2.85	1.9	.8	.29	5.2	23	81
52.2	5.25	3.38	2.58	1.2	.8	.29	3.2[b]	23[b]	80[b]
48.5	4.66	3.10	2.45	1.1	.7	.22	3.0	21	60
(Warming after standing at 30° twenty hours)									
45.1	3.75	2.78	2.38	.75	.47	.14	2.1	13	40
49.8	4.05	2.95	2.42	.97	.54	.25	2.7	15	69
53.7	4.40	3.10	2.45	1.3	.65	.27	3.7	18	76
54.9	4.50	3.18	2.48	1.3	.69	..	3.7	19	..
56.6	5.60	3.40	2.58	1.8	.72	..	5.0	20	.
57.1	8.12[a]	4.49	3.46	3.6	1.8	.33	10	50	92
57.4	3.45	3.42	3.42	0.02	0.00	.00	0.07	0.04	0.04
57.5	3.42	3.42	3.42		0		.04	.04	.04
58.5	3.35	3.35	3.35				.04	.04	.04
(Separate run, cooling)									
− 19.4		2.20							
− 34		2.16							
−149		2.12							
−180		2.12							
n-Docosyl Alcohol (Cooling)									
75.4	2.95	2.95	2.95	.18	.02	0.00	0.5	0.5	0.5
70.8	2.97	2.97	2.96[b]						
69.6	10.8	4.10	3.50	15	3.2	.40	43	90	110
69.6	15.9	4.81	3.76	21	4.2	.65	57[b]	115[b]	180[b]
69.5	14.2	5.10	3.88	14	4.0	..	40	110	..
68.8	13.0	5.10	3.84	12	3.2	.43	34	90	120
66.7	12.1	..	..	...	..	..	...	..	..
64.5	11.0	4.82	3.75	6.1	2.1	.41	17	60	115
64.5	9.20	4.65	3.50	3.1	1.8	..	8.5	50	..
64.1	7.76	4.48	3.38	3.1	1.6	..	8.5	45	..
62.2	6.65	4.40	3.18	0.50	..	..	...	..	..
58.4	6.60	..	3.12	.54	0.18	0.40	3.5[b]	14[b]	116[b]
56.8	6.40	..	3.08	.54	.50	.38	3.5	12	105
51.9	5.78	4.18	2.85	...	.40	.32	...	11	95
(Warming, after standing at 20° twenty hours)									
45.1	6.82	3.72	2.60	.68	.21	.02	1.9	6	60
55.2	5.98	4.36	3.00	.68	.47	.34	1.9	13	95
60.2	6.40	4.70	3.22	.68	.50	.38	1.9	14	105
64.5	6.88	5.08	3.48	.68	.54	.43	1.9	15	120
66.7	7.42	5.20	3.56	.68	.61	.43	1.9	17	120
68.1	9.56	7.00	3.68	1.7	1.0	.45	4.7	28	125
68.4	14.3	6.80	3.95	4.0	2.0	.47	11	57	130
68.9	4.07	3.40	3.08	0.68	0.39	.14	1.9	11	40
69.2	2.96	2.95	2.95	.2	0.00	.00	0.5	0.5	0.5
70.4	2.95	2.96	2.96	.2			.5	.5	.5

[a] When the same sample was rewarmed *immediately* a value of 19.5 was reached. [b] These data are used in Table II to calculate ε′.

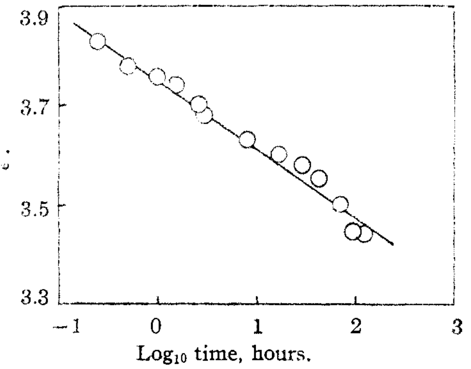

Fig. 8.—Dependence of dielectric constant of *n*-octadecyl alcohol on time at 0.25 kc. and 15.0°. The sample was rapidly cooled from 100 to 15° and held at this temperature.

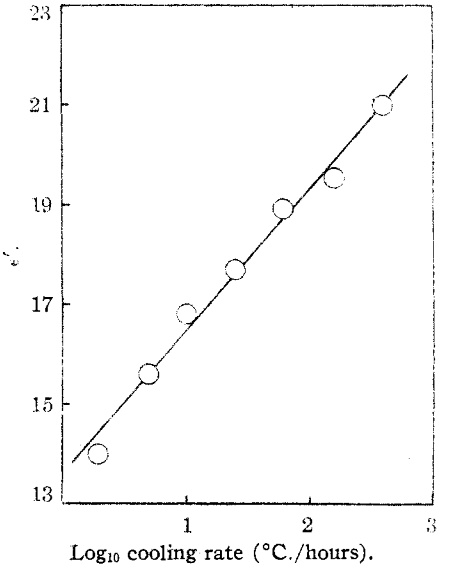

Fig. 9.—Dependence of maximum value of dielectric constant in waxy state on cooling rate of *n*-octadecyl alcohol. Data are for cooling rates as measured 1° above the freezing point and were obtained at 0.5 kc.

cooling rate measured 1° above the freezing point. The cooling and warming curves which were obtained concurrently with the dielectric runs are illustrated in Fig. 10. The dielectric data on impure *n*-dodecyl and *n*-octadecyl alcohols as received from the manufacturers are given in Fig. 11 to permit comparison of the properties of pure and impure materials.

Discussion of Results

n-Dodecyl alcohol (Fig. 1) shows no transitions in the solid, either in the cooling curve or in the dielectric data, and exhibits typical rotational freezing of dipoles on solidification. The conductivity of the liquid alcohol is less than that found by Frosch[3] (17×10^{-10} compared to 42×10^{-10}). Inasmuch as water was difficult to remove and in view of the appearance of the curve for the impure sample (Fig. 11) it is suggested that water, which forms a higher melting hydrate,[7] or other impurities may have caused previous investigators to obtain results which might be interpreted as indicating molecular rotation.

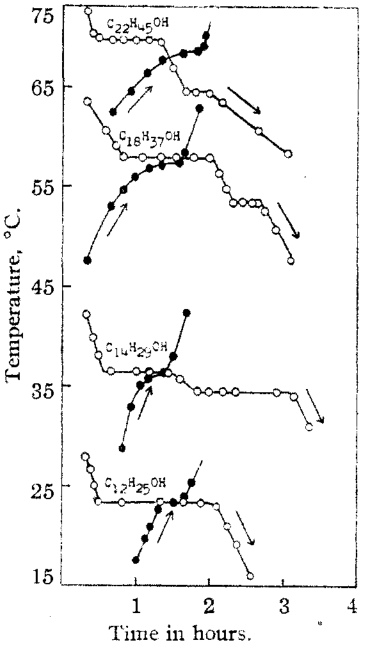

Fig. 10.—Temperature–time curves for *n*-dodecyl, *n*-tetradecyl, *n*-octadecyl and *n*-docosyl alcohols. Arrows indicate warming and cooling curves.

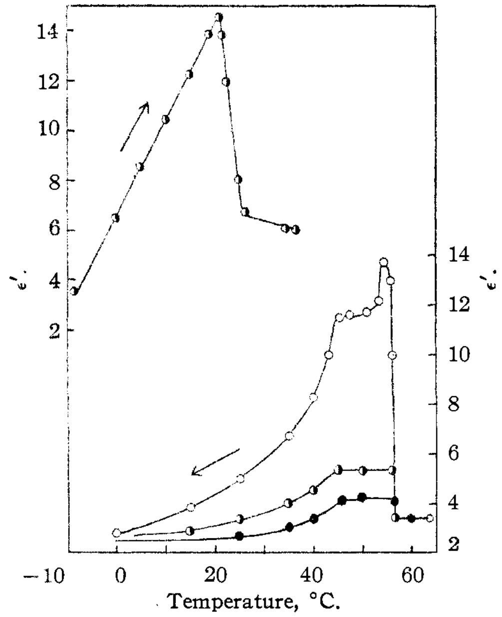

Fig. 11.—Temperature dependence of dielectric constant for impure alcohols. Upper curve, *n*-dodecyl alcohol, scale on left. Lower curve, *n*-octadecyl alcohol, scale on right. Hollow circles represent data at 0.5 kc., half-filled circles values at 5.0 kc., and filled circles data at 50 kc. Arrows indicate direction of temperature change.

n-Tetradecyl, *n*-octadecyl and *n*-docosyl alcohols show dielectric and thermal behavior similar to that of *n*-hexadecyl alcohol,[4] except that the waxy ranges are shorter, and that the transitions are not enantiotropic as previously reported.[10] The change of ϵ' with time at constant temperature (see Fig. 5, AB; Fig. 6, ABCD) indicates that the waxy state consists of a mixture of two solid phases, one of which is unstable. The alcohols change from clear-translucent to opaque-white on standing at constant temperature in the waxy state. The white regions appear first as small nuclei which slowly permeate the whole mass. This coexistence of two phases has been indicated by the X-ray measurements of Malkin[11] on *n*-hexadecyl alcohol, which simultaneously show the crystal spacings of the vertical and tilted forms.

The dielectric dispersion found in the waxy state of these alcohols may be quantitatively accounted for by Maxwell–Wagner polarization between two solid phases which we denote as α (unstable, clear) and β_2 (stable, white). The α form which crystallizes first from the liquid shows a much higher conductivity than the liquid or crystalline solid at low temperature. Frosch[3] arbitrarily pictured the two phase dielectric as two layers with interfaces parallel to the condenser plates, and, by the use of circuit analysis of the impedances, derived an equation for the observed capacitance as a function of the conductivities of the two phases. Using a similar method, we have obtained the following expression for the maximum observed dielectric constant

$$\epsilon'_{\mathrm{m}} = \epsilon + \epsilon(k_1 - k_2)^2/4k_1k_2$$

where k_1 and k_2 are the specific conductivities of the two phases, and ϵ is the dielectric constant arbitrarily taken as the same for each phase. The observed maximum in ϵ'_{m} appears for an optimum thickness of a given layer. In the derivation of the above expression it was assumed that $\epsilon'' > \epsilon'$, which is true only for a dielectric possessing conductivity other than that due to orientation loss. The alcohols show sufficient conductivity in the waxy state to cause ϵ'' to exceed ϵ' at moderately high frequencies, as may be seen in Table I. The supposition by Frosch that the liquid and solid alcohol coexist over long periods of time below the freezing temperature with the interface parallel to the cell plates is contrary to our observations, since the two solid phases are seen to coexist as a mixture over a range of temperature. Despite the fact that the material is not distributed in parallel slabs, there is enough similarity in the equivalent circuits to warrant application of the equation to the case where one phase is distributed as small platelets throughout the other. According to the equipotential surface theorem, the two-layer dielectric treated by Frosch is equivalent to a dielectric where the vertical slabs are split into any number of sheets, and arranged parallel to the condenser plates in any order. To a fair approximation these thin sheets may be subdivided into platelets of smaller area and distributed throughout the other material, thus approximating the two-slab model electrically as well as representing the mixture of solid phases observed experimentally. Hence, our equation should predict the behavior of the alcohols in the waxy state.

In order to apply the equation we take the dielectric constant of the liquid at the freezing point as ϵ and the specific conductivity of the α phase as that observed for the waxy state as a whole. Since the α phase conducts so much more than the β_2 and is much more abundant, this approximation is valid. The specific conductivity of the β_2 phase is assumed to be the same as that of the solid found a few degrees below the transition point after standing for a short time. These approximations are necessary because the phases cannot be physically separated. The data employed are marked with a "b" in Table I. In Table II ϵ'_{m} is compared with the value calculated by means of the equation.

TABLE II

COMPARISON OF THE CALCULATED AND THE OBSERVED VALUES OF ϵ'_{m}

	Calculated			Observed			
Alcohol	0.5	5	50 kc.	0.5	5	50	525 kc.
n-Tetradecyl	9.0	4.8		7.30	4.81		
n-Octadecyl	22	7.3	4.0	16.8	5.80	4.25	4.15
n-Docosyl	24	7.5	3.2	15.9	5.10	3.88	

In general, the calculated values tend to be somewhat high, but it is clear that the equation holds fairly well and that the Maxwell–Wagner polarization drops off sharply with increase in frequency. Considering the fact that no precise knowledge of the actual specific conductivities of each pure phase may be had, and that a rough model has been used, the agreement between observed and calculated values is satisfactory.

Now that analysis has shown the large increase in ϵ' to be due to Maxwell–Wagner effect, it is possible to interpret the data free of this phenomenon in terms of dipole rotation. Table II and Figs. 2, 3, 4 and 7 indicate that the Maxwell–Wagner effect is not important at 50 kc. for *n*-tetradecyl, *n*-octadecyl and *n*-docosyl alcohols. The persistence of a near-liquid value of the dielectric constant in the waxy state at this frequency clearly indicates that a state of dipole rotation exists. *n*-Octadecyl alcohol shows an increase of dielectric constant on freezing of roughly 20% even at 525 kc., and *n*-docosyl alcohol shows an increase of about 30% at 50 kc., but these increases may be accounted for largely by the increase in density of these compounds on solidification. It is possible that the values for *n*-docosyl alcohol are still slightly high at 50 kc. because of some persistence of the Maxwell–Wagner effect. *n*-Tetradecyl alcohol shows no increase in ϵ' on freezing, but, instead, falls off with decreasing temperature. This is probably due to the rather rapid transformation of the α-phase to

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(10) Meyer and Reid, THIS JOURNAL, **55**, 1574 (1933).

(11) Malkin, *ibid.*, **52**, 3739 (1930).

the more stable form during the cooling process. The true anomalous dispersion region is doubtless at a much higher frequency than any employed here, and should not be confused with the Maxwell–Wagner dispersion.

X-Ray studies show[2,11] that the oxygen atoms are arranged in a plane in the crystal, so that a sheet of rotating dipoles may be said to exist. Dipole rotation appears to be synonymous with rotation of the hydrocarbon chain. This is indicated by the cooling curves which show sharp transitions in the solid concurrent with the freezing out of dipoles, and by the X-ray data of Ott,[2] which show that the transition involves a change from rotation to non-rotation of the molecular chain. Molecular rotation about the long axis appears for shorter chain lengths in the alcohols (14 carbons) than in the corresponding hydrocarbons where 22 carbon atoms are required before rotation appears in the solid.[12]

The origin of the high conductivity attributed to the α phase, which is necessary to the elucidation of the dielectric behavior remains to be explained. The planes of hydroxyls in this phase, possessing rotational freedom through rotation of the entire molecules, seem to provide a possible site for the proton transfer mechanism of conduction treated by Stearn and Eyring.[13] Two important requirements are proximity of the hydroxyl groups to one another, and rotation of these groups such that an optimum configuration conducive to the transfer of a proton from a positive ion (*e. g.*, a hydronium ion) to a neutral molecule may occur with reasonable frequency in an applied field. Both requirements seem to be met in the α phase of the waxy state in the long-chain alcohols. No extensive sheets of hydroxyls possessing rotational freedom occur in either the liquid[14] or the low-temperature crystalline solid, and the relatively lower conductivity of these media should be due to the absence of the rotation required in the proton-transfer mechanism. Baker and Yager[15] have invoked a mechanism of proton transfer to explain the high d. c. conductivity of linear polyamides. Despite precautions, contamination of our samples with a very small amount of water is possible, but this could not account for the appearance of appreciable conductance solely in the waxy state, and not in the liquid or low temperature crystalline solid.

It is possible to correlate the properties of the vertical and tilted forms of long chain compounds with the dielectric changes and cooling curve data of the alcohols. The vertical forms found in long-chain compounds are those in which the carbon chains are perpendicular to the plane of the end groups, and the tilted forms are those in which the carbon chains are inclined at an angle to the plane of the end groups. The latter show shorter crystal spacings between the end groups than the former. For a number of long-chain compounds, including hydrocarbons, esters and acids, the vertical form tends to be clear, have a lower entropy of fusion per methylene group, and greater inter-chain mobility than the tilted form.[16] Thus it seems reasonable to assign to the clear, rotating α phase the vertical configuration. Ott[2] has found that the rotating molecules in *n*-tetradecyl and *n*-hexadecyl alcohols show the long crystal spacing, which proves that the α phases of these two substances are the vertical form. The irreversible conversion of α to β_2 in the waxy state, which is accompanied by a drop in ϵ' (Figs. 5 and 6) with simultaneous increase in opacity, is probably due to the slow conversion of the vertical (rotator) into the tilted (non-rotator) form; the slowness of the process is likely due to the high viscosity of the medium in which the molecules must move to achieve the configuration of lowest energy.

The transformation of the α phase proceeds during the freezing process in which α is formed from the liquid, and thus we may expect the maximum value attained by ϵ' at a given frequency to depend on the cooling rate. Figure 9 illustrates this effect for cooling rates between 2 and 400° per hour. The transformation of the α phase lowers the ϵ'_m. Differences in cooling rate as well as impurities may evidently be an important cause of discrepancies among the results on *n*-hexadecyl alcohol as reported by other workers.[3,4,17]

It is believed that a transition point is found in the solid because that portion of the α phase not yet converted into β_2 in the cooling process and retaining hexagonal close-packing of the chains collapses into what Ott terms a "monoclinic" lattice, with a considerable heat of transition. Since it has been shown[2] that the α form has the vertical configuration, it is plausible to suggest that the change to the "monoclinic" lattice at the transition point occurs while the chains are vertical. This would produce a form which we call β_1. It has been observed that the tilted form with the "monoclinic" carbon chain lattice is the stable form in the crystalline solid,[2,3] so that we might expect a slow rearrangement of β_1 into β_2 in the solid. Changes from vertical to tilted have been observed in the solid long chain iodides by X-ray techniques,[3] and an irreversible β_1 to β_2 transition in the solid similar to the present case has been found by polarization and coefficient of expansion measurements in ethyl docosanoate.[18] The data plotted in Fig. 8 for solid *n*-octadecyl alcohol at 15° at 0.25 kc. show that the dielectric constant drops slowly with time over a period of five days, and afford a strong indication of the expected β_1 to β_2 transition. Further evidence that a change is taking place in the crystalline solid below the transition point is afforded by the fact that the

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(12) Müller, *Proc. Roy. Soc.* (*London*), **A138**, 514 (1932).

(13) Stearn and Eyring, *J. Chem. Phys.*, **5**, 113 (1937).

(14) Pierce and Macmillan, THIS JOURNAL, **60**, 779 (1938).

(15) Baker and Yager, *ibid.*, **64**, 2171 (1942).

(16) King and Garner, *J. Chem. Soc.*, 1368 (1936).

(17) Higasi and Kubo, *Bull. Chem. Soc. Japan*, **12**, 326 (1937).

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

dielectric data obtained on warming differed greatly in the maximum value of ϵ' attained, the difference depending on the time the solid had been allowed to stand. Thus, the highest value at 0.5 kc. reached on re-warming *n*-octadecyl alcohol which had been allowed to stand twenty hours at about 25° was 8.12 (Fig. 3), but immediate rewarming yielded a value of 19.5. A similar effect was found for *n*-docosyl alcohol. Finally, changes in melting and freezing point values give evidence for the β_1 to β_2 transition in the solid. For example, *n*-octadecyl alcohol which had stood overnight at room temperature remelted at 57.4° (Fig. 10) while that which was rewarmed immediately melted at 57.7°. An even more pronounced effect involving a temperature difference of 0.9° was observed for *n*-docosyl alcohol. These facts are in accord with the principle that those molecules which rotate in the solid tend to melt at a somewhat higher temperature than their non-rotating counterparts.[19] The thermal (Fig. 10) data illustrate the difference between freezing and melting point nicely.

The general picture proposed for the phase changes in these alcohols is the following: *n*-Dodecyl alcohol crystallizes directly into a stable form, but the higher alcohols crystallize from the liquid to a more or less transparent α form, which shows rotation about the long molecular axis. The α modification is unstable and begins to change to a more stable non-rotating form, β_2. This system, a non-equilibrium of two allotropic modifications, has the ability to exhibit Maxwell–Wagner polarization since the α phase is a conductor. At a transition point below the freezing point the α form which has not been converted to β_2 transforms into β_1. β_1 is not stable but slowly changes to the stable β_2 form. The β_2 forms melt below the original freezing point, as would be expected, since they do not possess molecular rotation.[19]

The chain length of fourteen carbon atoms at which molecular rotation is possible in the alcohols is shorter than for which it has been observed in other types of long molecules, which will be discussed in a later paper. In conformity with previous work, there is no indication that the rotation is that of the hydroxyl around the C—O bond.

Summary

The dielectric constants and loss factors of *n*-dodecyl, *n*-tetradecyl, *n*-octadecyl and *n*-docosyl alcohols have been measured over a wide range of temperature and frequency in order to investigate the possibility of molecular rotation in the solid forms. When carefully purified, *n*-dodecyl alcohol gave no evidence of molecular rotation in the solid state. The other three alcohols, on cooling of the liquid, froze to waxy solids possessing dielectric constant values so high as to show the presence of strong Maxwell–Wagner polarization. The values were dependent on the cooling rate. An equation approximately representing the observed dielectric behavior of the waxy solid has been developed on the assumption of the coexistence of two solid phases of very different electrical conductivities. The two phases formed on freezing consisted of an unstable α phase observed to be translucent together with a small amount of a stable, opaque β_2 phase, which increased in amount with the passage of time. The α phase was found to show rotation of the molecules around their long axes, and its high electrical conductivity was attributed to proton transfer facilitated by the molecular rotation. On cooling, the α phase showed a transition to an unstable β_1 phase, in which the molecules did not possess rotational freedom. The α phase in *n*-tetradecyl alcohol appears to be less stable than that in *n*-octadecyl alcohol. The β_1 phase gradually changed to the β_2, which, possessing no rotational freedom, melted slightly below the freezing point. The setting-in of some dielectric dispersion just below the transition point was attributed to incompleteness of the conversion from β_1 to β_2. Differences in results obtained on warming and on cooling were related to phase changes in the solid.

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[19] Baker and Smyth, *Ann. New York Acad. Sci.*, **XL**, 447 (1940).