On the Dielectric Anomaly of n-Higher Alcohols in the "Waxy State"

By

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Introduction

Of the dielectric anomaly of n-higher alcohols in the "Waxy state" stable at temperatures just below the melting point, Hoffman and Smith[1] attributed the origin to Maxwell–Wagner polarization. Meakins and Mulley[2] found abnormally large values of dielectric absorption and of dispersion of the dielectric constant at low frequencies, at temperatures below that of the waxy state, and explained the facts by the presence of hydrogen–bonded chains of hydroxyl groups capable of reversing their directions. It appears that they supposed the same to be true even in the waxy state, but gave no explanation for the dielectric absorption which is especially abnormal in the waxy state. On the other hand Asai and his cooperators[3] considered that the high value of dielectric constant of n-higher alcohols is only superficial and should be explained with Cole's theory[4] of the conductive dielectric.

The purpose of the present paper is to describe the author's experimental study to test the above theories. If Asai's opinion is correct the dielectric constant of a n-higher alcohol must vary with electrode seperation of the condenser as Cole pointed out.[5][6] Therefore the present author measured the dielectric constant of cetyl alcohol and octadecyl alcohol with different electrode seperation from 1.2 mm to 6.7 mm at frequncies 2 Kc/s and 0.6 Kc/s, but could not find significant variation. For the purpose of studying the dielectric mechanism it is often useful to determine the relation of the real part ε' and the negative imaginary part ε'' of the complex dielectric constant[7], so the author measured the two values in the waxy state and plotted a Cole–Cole diagram. The result shows that the dielectric anomaly of n-higher alcohols in the waxy state must be attributed mainly to the orientational polarization as was advocated by Meakins and Mulley rather than to Maxwell–Wagner polarization.

Experimental Procedure

The apparatus and the experimental procedures adopted were generally the same as those described in the preceding paper.[8] The sample was put in a condenser with the electrodes insulated by three spaceres. The thickness of the spacers was 1.27 mm, 3.17 mm, 5 mm and 6.7 mm respectively in the four experiments.

The temperature dependency of the dielectric constant and the electric conductivity was measured in the heating or cooling stage at 2 Kc/s or 0.6 Kc/s. The frequency dependency of the dielectric constant and the electric conductivity was measured at a fixed temperature of the waxy state in the heating or cooling stage. For the measurement a low frequency capacity resistance bridge, and RC type oscillator of frequency range 20 c/s–20 Kc/s were used.

The direct conductance error of ε'', namely the additive contribution to ε'' from dc conductance, was corrected by subtraction of the dc conductance G_{dc} from the total conductance $G(\omega)$ at each frequency, the expression used being

$$\varepsilon'' = (G(\omega) - G_{dc})/\omega C_0,$$

the values of G being expressed in $\mu\mu$ mho and of cell capacitance C_0 in $\mu\mu f$. The value G_{dc} was measured simultaneously by a vacuum tube electrometer.

The samples used were cetyl alcohol, m.p. 48.7°C, and octadecyl alcohol, m.p. 54.9°C containing some impurities.

Experimental Results and Discussion

(1) *The effect of the electrode seperation*

The effect of the electrode seperation d on the real part ε' is shown in Fig. 1 and Fig. 2. Fig. 1 is the temperature dependency of the real part ε' of the complex dielectric constant of cetyl alcohol in the heating stage and 2 Kc/s measured at several electrode seperations, Fig. 2 is that of octadecyl alcohol in the cooling stage and 0.6 Kc/s.

In these figures the maximum of the curve is highest at the lowest electrode seperation 1.27 mm, but it may be due to the experimental error. At any rate the author could not find the significant variation with electrode seperation. Neither could he find any effect of the electrode seperation on the negative imaginary part ε''. Auty and Cole[5] found a remarkable effect due to the electrode polarization in the conductive ice at frequencies below 1.5 Kc/s, and that it was negligible when the electrode seperation
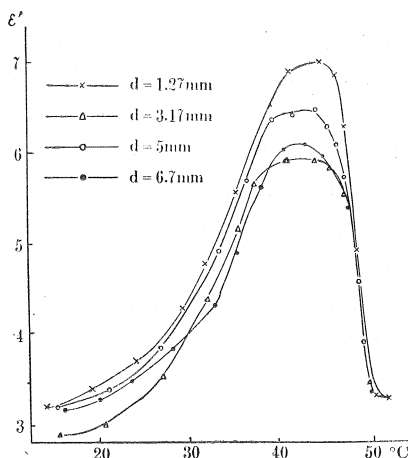

Fig. 1.

Temperature dependency of the real part ε' of the dielectric constant of cetyl alcohol in the heating stage and 2 Kc/s measured at several electrode seperation.
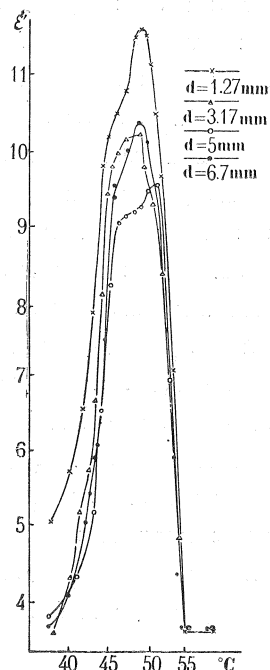

Fig. 2.

Temperature dependency of the real part ε' of the dielectric constant of octadecyl alcohol in the cooling stage and 0.6 Kc/s measured at several electrode seperation.

exceeded 6 mm. And so the dielectric anomaly of *n*-higher alcohols in the waxy state does not seem to be a surface effect in the sense of Cole's theory but principally a volume property at least at frequencies above 0.6 Kc/s. The reason why the conductive *n*-higher alcohols in the waxy state do not show the effect of electrode polarization similar to that of the conductive ice may be the difference of the mechanisms of the conductivity. Of the *n*-higher alcohols the effect may appear only at much lower frequencies.

(2) *Relation of* ε' *and* ε''

It was very difficult to measure the values of capacity and total conductance at several frequencies and that of dc conductance of the condenser at a fixed temperature of the sample, but the author contrived to finish the measurement as quickly as possible. The results obtained in the heating stage are shown in Fig. 3 and Fig. 4, each graph being a circular arc with its center a little below the ε' axis. At lower frequencies experimental errors became larger and below a certain limiting frequency neither ε' nor ε'' could be measured.

The value G_{dc} for the case of Fig. 3 ammounted to 20 % of the total conductance at frequency 20 Kc/s, and to 40 % at frequency 0.5 Kc/s. For the case of Fig. 4 these values were 8 % and 35 % respectively. Sometimes the diagram deviated from the circular arc at lower frequencies as shown in Fig. 5.

At any rate the fact that the relation of ε' and ε'' is indicated by an circular arc, excepting the case of much lower frequencies, seems to show that the dielectric
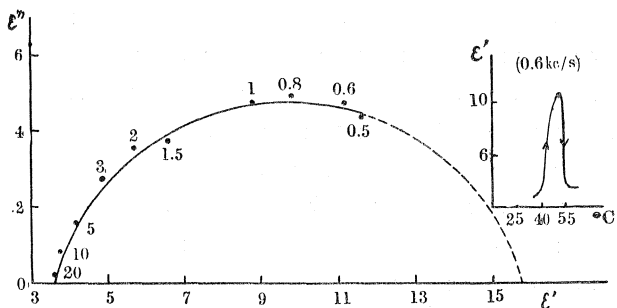

Fig. 3.

Complex dielectric constants of octadecyl alcohol at the temperature (49.5°C) shown in the ε'–T curve in the heating stage.
Electrode seperation : 1.27 mm
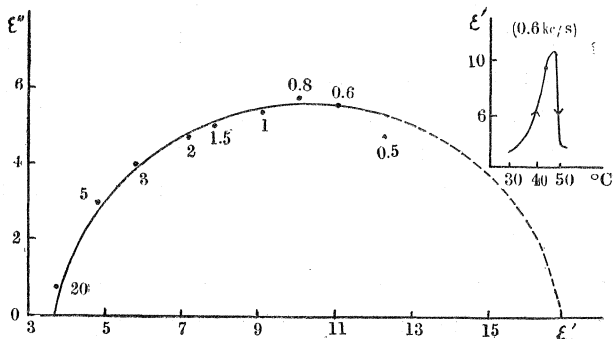Numbers beside points are frequencies in Kc/s

Fig. 4.

Complex dielectric constants of cetyl alcohol at the temperature (42.5°C) shown in the ε'–T curve in the heating stage.
Electrode seperation : 1.27 mm
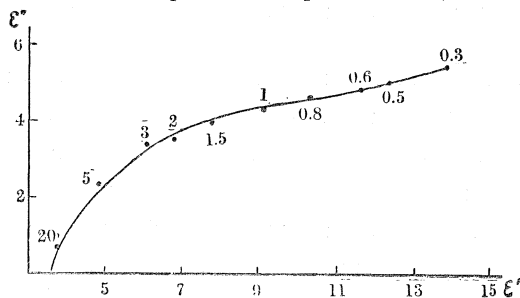Numbers beside points are frequencies in Kc/s

Fig. 5.

Complex dielectric constants of octadecyl alcohol at 49°C in the heating stage.
Electrode seperation : 1.27 mm
Numbers beside points are frequencies in Kc/s.

mechanism is to be attributed to the orientational polarization. Of course it is important to recognize, as Cole pointed out,[7] that the circular arc does not necessarily originate from the orientational polarization. That is, a semicircular locus results from Maxwell–Wagner polarization when we assume that the dielectric constants and electric conductivities of the two phases of a composite are independent of frequencies. But in this case it does not seem right to admit the above assumption. Furthermore the locus is not a semicircle but a circular arc with its center a little below the ε' axis. And so it is not unnatural to assign the orientational polarization of a little broader distribution in relaxation time. Such mechanism may perhaps be attributed to the orientation of the hydroxyl group alone and not to that of the entire molecule, as was advocated by Meakins and Mulley for temperatures below that of the waxy state. For comparison a Cole–Cole diagram based on the data of Meakins and Mulley,[2] is shown in Fig. 6.
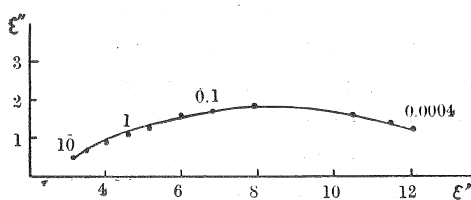

Fig. 6.
Complex dielectric constants of octadecyl alcohol at 20°C (Meakins and Mulley)
  Electrode seperation : 2 mm
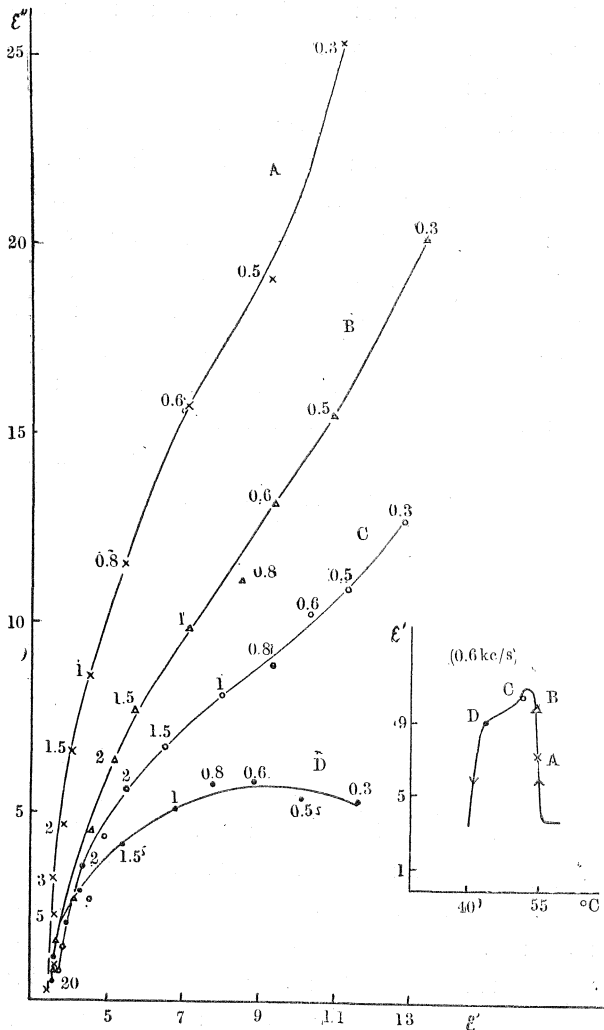 Numbers beside points are frequencies in Kc/s.

The chief differences between Fig. 3 and Fig. 6 are, (1) the dielectric dispersion for the waxy state is displaced to higher frequencies, (2) a larger distribution in relaxation time is shown in Fig. 6 compared to that of Fig. 3, and (3) considerable difference in magnitude of ε'' which results from (2).

The absorption at much lower frequencies shown in Fig. 5 may be due to some causes such as the following.

(1) Maxwell–Wagner polarization resulting from the situation of the conductive hydrogen-bonded chains in a non-conducting matrix as was advocated by Hamon and Meakins.[9]

(2) Electrode polarization of Cole's theory.

(3) The orientation of entire molecule rather than that of the hydroxyl group alone as in the cooling stage to be explained subsquently.

But the author has not been able so far to confirm the real cause.

The measurements had to be carried out more quickly in the cooling stage than in the heating stage because of the difficulty of maintaining the equilibrium in the waxy state. Hence the experimental errors were larger in the cooling stage. Fig. 7 is the diagram for the cooling stage and shows a conspicuous variation with temperature as compared with that for the heating stage.

As was also described by some previous investigators[1][3][10] the aspects for the cooling stage are quite different from those of the heating stage as are clearly seen in Figs. 8, 9 and 10, which respectively show the D.C. conductivity, A.C. conductivity, and dielctric constant ε' as functions of temperature.

Fig. 7.
Complex dielectric constants of octadecyl alcohol at the
temperatures shown in the ε'–T curve of the cooling stage
  Electrode seperation : 3.17 mm
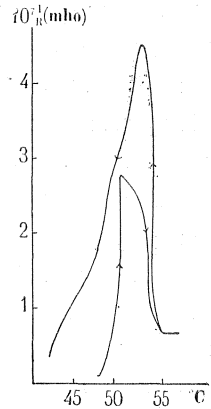 Numbers beside points are frequenies in Kc/s.

Fig. 8.
Temperature dependency
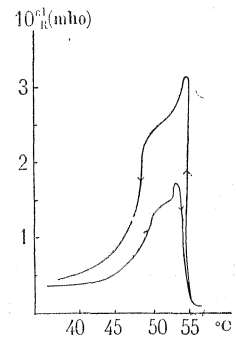of D. C. conductivity of
octadecyl alcohol.

Fig. 9.
Temperature dependency
of A. C. conductivity of
octadecyl alcohol (2 Kc/s).
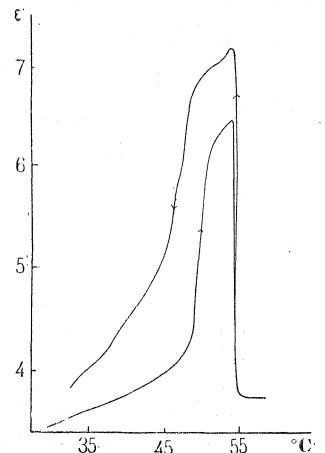
Fig. 10.
Temperature dependency
of dielectric constant of
octadecyl alcohol (2 Kc/s.)

For the case of curve D in Fig. 7 the value G_{dc}
ammounts to 12 % of the total absorption con-
ductance at frequency 20 Kc/s, and to 25 % at 0.5
Kc/s. For the case of curve A these values are
18 % and 19 % respectively. Curve D is very close
to a circular arc, and the shape seems to be
attributable to the same orientational polarization
as in the heating stage. In curve C and B the
deviation from the circular arc is conspicuous in

the lower frequencies, and ε'' has values greatly differing from the corresponding values in curve D, while there is little difference in the values of ε'. Curve A is roughly linear, and in this case ε' is a little smaller than in B and C.

For these phenomena, too, some of the three causes mentioned for Fig. 5 may be responsible. But cause (2), namely electrode polarization, seems to be unimportant, because large values of ε' and ε'' were always obtained irrespective of the electrode seperation. On the other hand cause (1), namely Maxwell–Wagner polarization, is also unlikely to happen inasmuch as only ε'', not ε', varies markedly with temperature.

Therefore we considered cause (3), that is, as the temperature becomes higher and the frequency lower the orientation of the entire molecule becomes more likely to occur than that of the hydroxyl group alone. Because though the orientation of the entire molecule induces nearly the same amount of polarization as that of the hydroxyl group alone, the former will produce larger values of ε'' than the latter as a result of the difference of their activation energies, or relaxation times. This is seen from the Debye equations.

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2} \tag{1}$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \tag{2}$$

which, combined, gives

$$\varepsilon'' = (\varepsilon' - \varepsilon_\infty)\omega\tau \tag{3}$$

showing the relation mentioned above.

Furthermore, ε' does not decrease so markedly by the increasing of τ, because, the author believes, the value of ε_0 in (1) increases with increse of τ, which in turn may be attributed to the increasing of the magnitude of the effective dipole moment of the hydroxyl group resulting from the orientation of the entire molecule.

Besides the assumption (3) seems natural when the difference in magnitude of the inertia of entire molecule and that of the hydroxyl group alone is kept in mind.

Causes (1) and (2) may, however, also be significant at frequencies much lower than those used in the author's experiments.

References

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