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On the Dielectrics treated by an Electric Field III. The Dielectric Properties of α-Monostearin

By

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Introduction

Many authors(1)—(7) have hitherto shown interested in the anomaly of the dielectric properties of n-higher alcohols. The present author found anew peculiar effects of an electric field on these substances.(8)—(10) He was not a little interested with the fact, because such a fact can not be found in most other substances, and also because it gave him the idea that by studying it some hints might be obtained to the explanation of the anomalous dielectric properties of n-higher alcohols themselves of which a conclusive theory seemed to be still lacking.

Now it was known by Bhide(11)*, Crowe and Smyth(12) that α-monostearin has dielectric anomaly similar to that of n-higher alcohols. So the present author studied experimentally whether α-monostearin shows under an electric field any effect similar to that of n-higher alcohols. The results obtained generally seemed to indicate that it does.

Experimental Procedure

The apparatus and the experimental procedure adopted were generally the same as those described in the preceding report(8) but different in some small respects. Therefore an outline may not be out of place here. The sample was put in a plate condenser with the electrodes (diameter: 7.4 cm) insulated by three glass spacers (thickness: 1.4 mm). Since the condition of the solidification of the melted sample seriously affected the experimental results and also slow cooling fails to cause solidification of the sample owing to the generation of heat by the electric current, the following procedure was adopted except in special cases.

The liquid sample was rapidly cooled to the temperature of melting ice under an electric field or otherwise and placed in a desiccator of room temperature for one day. After that the temperature dependency of the dielectric constant and the conductivity was measured. For the measurement a low frequency (2 K. C.) capacity resistance bridge was used and the equivalent resistance was taken on the assumption

* The author has had no opportunity of seeing Bhide's original paper.

that the dielectric would behave as a capacity and a resistance connected in parallel. R C type oscillator was used and the balancing was done by an vacuum tube voltmeter as in the previous experiment. The average rate of warming was about 0.2° per minute.

Experimental Results and Discussions

Crude commercial sample of α-monostearin was used in every case. Its m.p. was 58° greatly differing from the 73° of the pure sample. But it seemed to be good enough for qualitative study of the effect of an electric field. Curve (1) in Fig. 1 shows the temperature dependency of the dielectric constant of the sample solidified without an electric field. Its transition point could not be found on account of its impurity. The maximum of the curve corresponds to $\varepsilon=57$.

Crowe and Smyth [12] reported that the apparent dielectric constant at 0.5 K. C. had been of such a magnitude (above 30) that the bridge could not been balanced.

(I) A sample rapidly solidified without an electric field was warmed to 40° and after a D. C. voltage of 800 V was applied to it for one hour, then the substance was cooled. Curve (2) in Fig. 1 is for this sample. It is seen that the dielectric constant of the sample is markedly below the normal value. (This is called the D.C. effect)

(II) The dielectric constant of the sample solidified under rapid (2 minutes) cooling with an A.C. voltage of 1000 V was seen to be above the normal value (This is called the A. C. effect) as shown by curve (3) in Fig. 1. Its maximum value corresponds to $\varepsilon=95$. Occasionally it reached even to $\varepsilon=140$.

(III) When the sample was solidified rapidly (2 minutes) under a D. C. voltage of 1000 V, its curve was coincided with curve (1) in Fig. 1 within the experimental error.

For the electric conductivity similar effects were also found as shown in Fig. 2. Curve (2) in

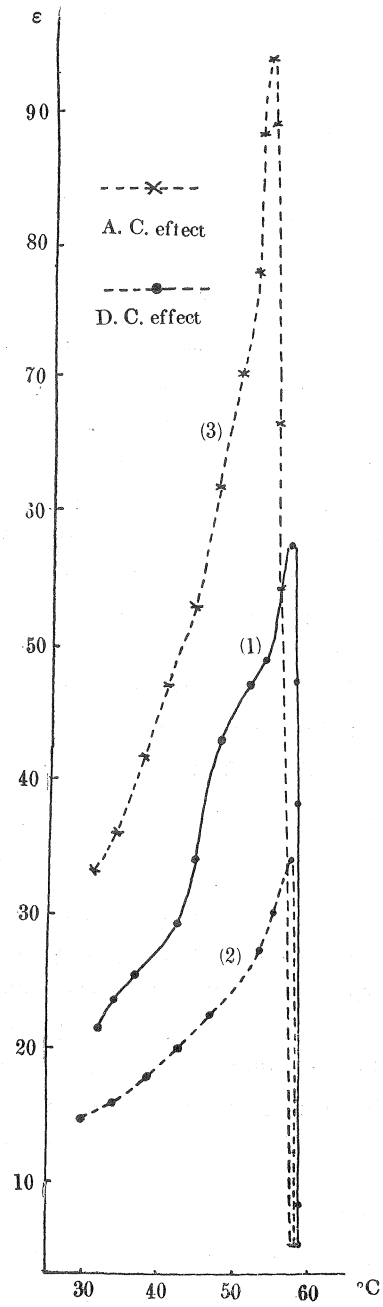

Fig. 1. D. C. effect and A. C. effect for the dielectric constant (2 K. C.)

Fig. 2 is for the D. C. effect and curve (3) corresponds to the A. C. effect. D. C. effect and A. C. effect are quite analogous to those of cetyl alcohol mentioned in the previous report.[8]

In order to find out the causes of the above phenomena (I), (II), (III) the following procedures were carried out.

(1) The electric current conducted by the sample during rapid cooling under an electric field was measured. The result is shown in Fig. 3. The curves of D. C. and A. C. are quite different though the voltage was same (1000 V) in each case.

(2) When the sample which had shown the D. C. effect was melted and then immediately solidified, some part of the D. C. effect was found remaining.

(3) When the D. C. voltage was applied to the sample in the liquid state for 2 minutes and removed as soon as the solidification began, the D. C. effect was not seen.

(4) The sample solidified rapidly without an electric field was warmed to 40° and, after a D. C. voltage of 800 V was applied to it for one hour changing its direction every thirty seconds, cooled rapidly. The D. C. effect was seen.

(5) The sample which had shown the A. C. effect was melted, then immediately solidified. The A. C. effect was absent.

(6) When the A. C. voltage was applied to the substance in the liquid state for 2 minutes and removed as soon as the solidification began, the A. C. effect did not appear.

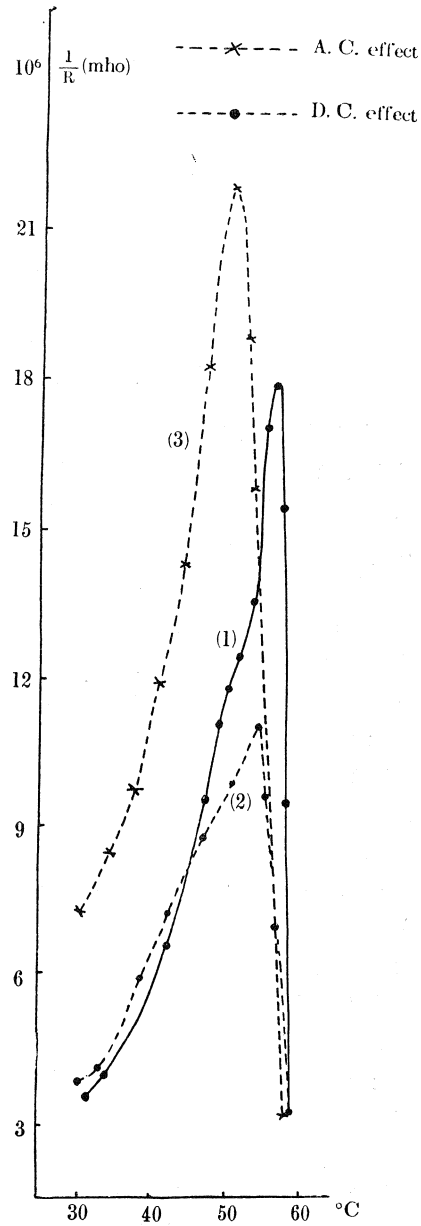

Fig. 2. D. C. effect and A. C. effect for the electric conductivity.

The causes of the facts (I), (II), (III) must be considered from the preceding experimental results. But before that, we must refer to the opinions of earlier researchers about the dielectric anomaly of alcohols and monoglycerides.

According to Hoffman and Smyth[3] the dielectric anomaly of the n-higher alcohol

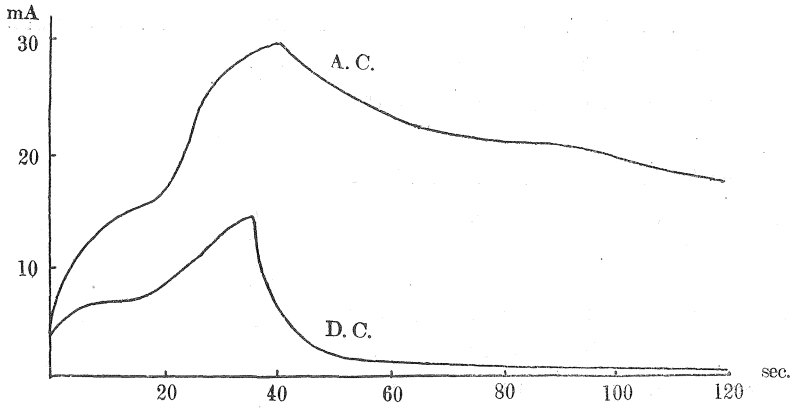

Fig. 3. Variation of the electric current with time.

was attributed to Maxwell-Wagner polarization between two solid phases having different values of conductivity and of dielectric constant. On the α-monoglyceride Crowe and Smyth [12] could not find two phases, but they adopted again the Maxwell-Wagner's theory to explain the dielectric anomaly. They considered that the application of an electric field would induce a relatively large displacement of charge in each microcrystal due to displacement of protons, and when the field changes direction this displacement would be reversed. Thus each crystal acts as a macroscopic dipole. Such spatial polarization mechanism seemed to be similar to that of ordinary Maxwell-Wagner polarization and they expected that the observed effect should be dependent to some extent upon the sizes and shapes of the microcrystals. And they concluded that the similar behavior of the long chain alcohol might also be explained in this manner.

On the other hand Asai and others [7] recently disagreed with the oppinion of Smyth and his coworker and considered that the high value of the dielectric constant of n-higher alcohol is only superficial and is due to the higher electric conductivity of its molecular rotating phase and should be explained with Cole's theory [13] on the conductive dielectric.

It seems to the present author that the mechanisms proposed by the two groups of authors are both reasonable, not contradictory, and the only question is the extent to which each of the two mechanisms contributes to the result.

Let us now discuss the causes of the phenomena (I), (II), (III). The phenomenon (I) (that is D. C. effect) is probably due to the decrease of hydrogen bonds resulting from the proton transfer in the solid. The effect of the space charge near the electrodes due to the D. C. current is not likely to be principal cause, because in the case of experiment (4) the space charge was not very conspicuous but the D. C. effect was marked. The phenomena (2) and (3) also seem to support such supposition. As for the phenomenon (II) (that is A. C. effect) we must first consider the effect of ions produced by the high A. C. voltage, but this probably is not the principal cause,

for in the experiment (6) though ions might have been present, A. C. effect was not seen. The A. C. effect seemed to be remarkable only when the A. C. voltage was applied continuously during the solidification. We may adopt with equal satisfaction either Smyth's or Asai's opinion and explain the A. C. effect by the increasing of the electric conductivity due to the proton transfer resulting from the treatment under an alternating electric field. In short the increasing of the proton transfer seems to be the principal factor of the A. C. effect. Now in Fig. 3 it is seen that even in the moment just before A. C. voltage was removed the current retained considerable strength. So the molecules seem to crystalize in the state of vigorous rotation, and the resistances to the rotation is seemed to decrease after the solidification.

This may explain the increasing of the proton transfer. The phenomena (5) and (6) also seem to support such explanation. Yet this does not seem conclusive, when we consider the fact that in the case of cetyl alcohol the A. C. effect remained almost unchanged if the sample which had shown the A. C. effect was melted and solidified again. Perhaps we should explain the A. C. effect by the same mechanism for both cases of cetyl alcohol and α-monostearin. Therefore it may be well to adopt for α-monostearin the same hypothesis as for cetyl alcohol.[8] That is, A. C. effect of α-monostearin is due to the increase of the number of hydrogen bonds, or the increase of the size of the microcystals resulting from the action of an alternating electric field. But we assume, in order to explain the phenomenon (5), that, unlike cetyl alcohol, α-monostearin lacks the stability in the liquid state.[8] Of course we assume that the hydrogen bonds will not decrease by the proton transfer of the alternating current as in cetyl alcohol.[9]

Finally the phenomenon (III) may be explained as follows. The orientation of microcrystals by the electrostatic field will increase the proton transfer, but the loss of the hydrogen bonds by the D. C. current will decrease the proton transfer, and the two effects will just cancel each other so that no conspicuous effect can remains.

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