

On the Dielectrics treated by an Electric Field. I

メタデータ	言語: eng 出版者: 公開日: 2017-10-03 キーワード (Ja): キーワード (En): 作成者: 井田, 光雄 メールアドレス: 所属:
URL	https://doi.org/10.24517/00011530

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On the Dielectrics treated by an Electric Field I.

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(Received 21. Dec. 1953)

Introduction

With respect to the properties of the dielectrics solidified under an electric field, several researches have been made in connection with the electrets.⁽¹⁾

For some years the author has been studying the properties of the dielectrics generally treated by an electric field, and a report of his experiments together with the discussion of the dielectrical properties concerning cetyl alcohol, lauryl alcohol and amilan (polymer) which have hydrogen bonds are given below.

Experimental Procedure

The arrangement of the experimental apparatus is illustrated schematically in Fig. 1.

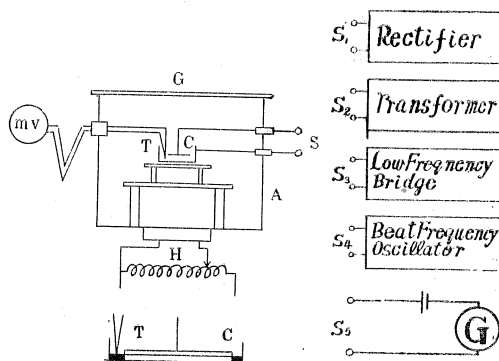


Fig 1. Arrangement of the experimental apparatus

The sample was placed in the plate condenser C, whose electrodes (diameter : 7.4 cm) were insulated by three glass spacers (thickness : 1.4 mm).

The surfaces of the electrodes were nickel plated. The capacity of the condenser was approximately $34\mu\mu$ F. The condenser was put into an air thermostat A. The temperature of the sample was recorded by a copper constantan thermo-junction T.

Since the condition of the solidification of the melted sample affected the experimental results, the following procedure was taken except in special cases. After removing the cover G the current of the heater H was opened, and the sample was cooled spontaneously.

When the cooling was made under an electric field, switches S and S₁, or S and S₂ were closed, and opened after one hour.

All measurements were mad one day after the solidification. In order to measure the dielectric constant and electric conductivity at the same temperature, switch S was

connected with S_3 , S_4 , S_5 by turns.

First, S was connected with S_3 , and the dielectric constant was measured by a low frequency bridge under the frequency 2 K. C. per second.

The balancing of the bridge was detected by the method as shown in Fig. 2 which can read the maximum current by a microammeter.

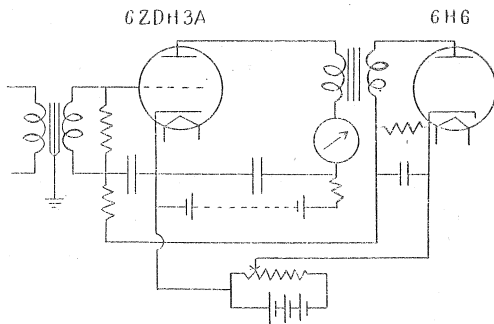


Fig. 2. Null detector

Nextly, S was connected with S_4 and the measurement of high frequency 3 M. C. was made by a heterodyne beat method (Fig. 3).

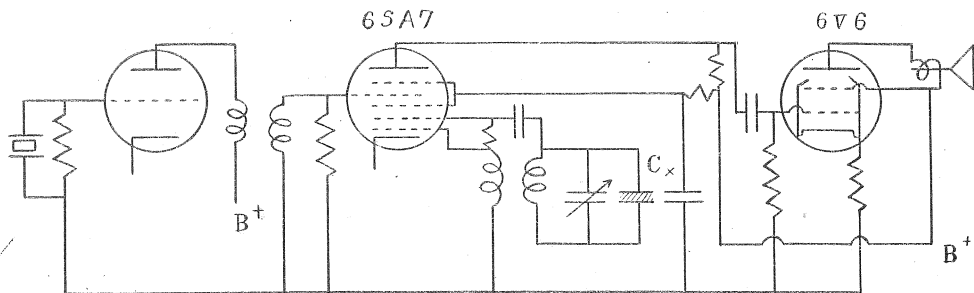


Fig. 3. Beat frequency oscillator

Finally S was connected with S_5 and the electric conductivity was measured by a galvanometer.

The time rate of the temperature rise was so small that the time necessary for the sample to rise from the room temperature to the melting point was about four hours. Therefore the effect of the current, which was resulted when the sample solidified under an electric field was warmed again, perhaps could be neglected. (2), (3), (4)

Experimental Results and Discussions

Cetyl alcohol

Crude cetyl alcohol was once fractionated at a reduced pressure using a fractionating tube of 1 m in length. The melting point was 48.5°-49°.

The fact that the dielectric constant of the sample solidified under a D. C. electric

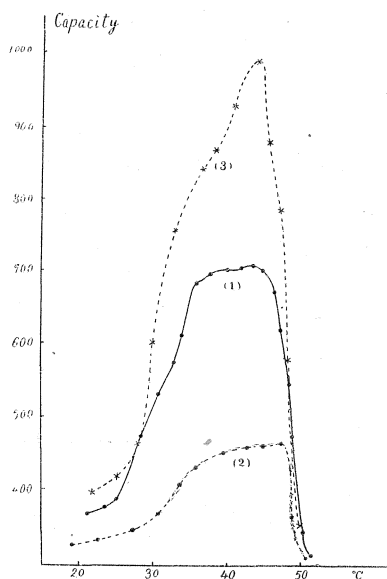


Fig.4. D. C. effect and A. C. effect for the dielectric constant (2. K. C.)

field will decrease from the normal value (say D. C. effect) has already been reported. * The author carefully confirmed this. And the fact that the dielectric constant of the sample solidified under an A. C. (60cycle) electric field will increase above the normal value (say A. C. effect) was newly found. Both effects are shown as in Fig. 4.

Curve (1) is for a sample solidified without electric field, curve (2) and (3) corresponds respectively to the case where the sample was solidified under the electric field of D. C. 1 KV or A. C. 1 KV. Fig. 4 is for the measurements by the frequency 2 K.C. In the case of the frequency 3 M. C. per second, both D. C. and A. C. effects could not be found. For the electric conductivity similar effects were also found as shown in Fig. 5 and Fig. 6.

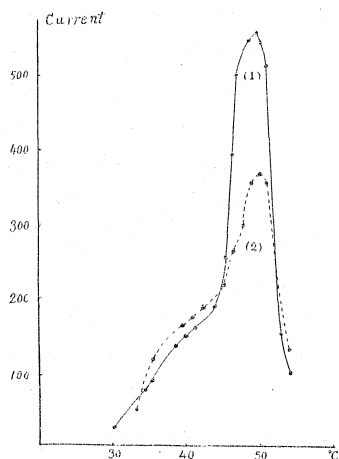


Fig. 5. D.C. effect for the electric conductivity

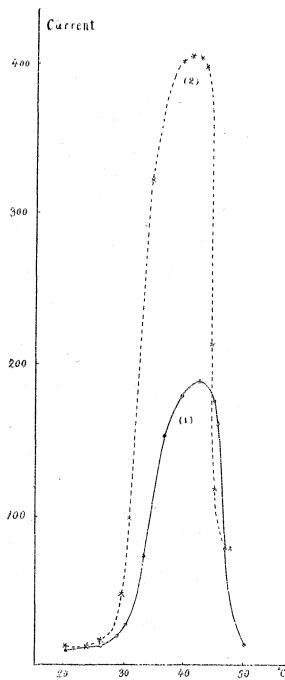


Fig. 6. A.C. effect for the electric conductivity

(2) in Fig. 5 is for D. C. effect, and curve (2) in Fig. 6 corresponds to A.C. effect.

* K. Asai : Lecture at the Phys. Soc. Meeting at Osaka, November, 1950.

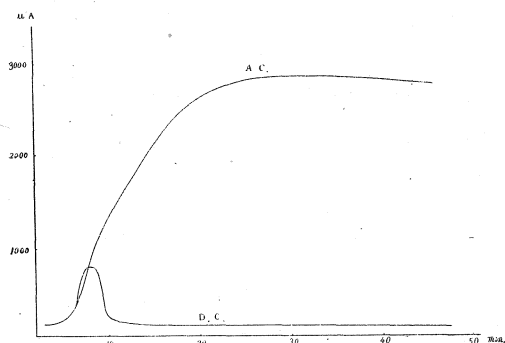


Fig. 7. Variation of the electric current with time

In order to find out the causes of the D.C. or A.C. effect, the following procedures were attempted.

(1) The electric current with the sample under an electric field was measured. The result is shown in Fig. 7. The curves of D.C. and A.C. are quite different, in spite of the same voltage 900 V.

(2) When the sample which had shown D.C. effect was melted and solidified again, D.C. effect almost remained unchanged.

(3) When the D.C. electric field was applied to the sample in liquid and removed as soon as the solidification began, D.C. effect was not seen.

(4) In case the D.C. electric field was applied in the solid state (27°C or 40°C), D.C. effect was seen.

(5) A sample which had shown D.C. effect was melted and solidified under an A.C. electric field. A.C. effect was seen.

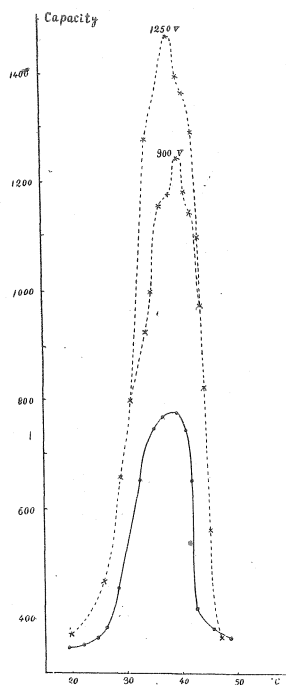


Fig. 8. Variation of A.C. effect with voltage (2 K.C.)

(6) When the sample which had shown A.C. effect was melted and solidified again, A.C. effect remained almost unchanged.

(7) When the A.C. electric field was applied in liquid and removed as soon as the solidification began to take place, A.C. effect was seen, though slightly.

(8) When the A.C. electric field was applied in solid, A.C. effect was not conspicuous. The effect seems to be most remarkable if the A.C. electric field was applied continuously from the liquid to the solid.

(9) The higher the A.C. voltage, the larger was the A.C. effect as shown in Fig. 8.

(10) When a sample which had shown A.C. effect was melted and solidified under an D.C. electric field, some D.C. effect took place.

(11) The samples used in the experiment were not extra pure, but it seemed that the less pure, the smaller was the effect of the electric field.

From the preceding experimental results the author came to a conclusion as follows.

(1) D.C. effect is due to the decrease of hydrogen

bonds resulted from the proton conduction in solid.

(2) A. C. effect is due to the increase of hydrogen bonds resulted from the action like a stirring by A. C. current when the liquid solidifies.

(3) Moreover, for the explanation of the experimental results, it is necessary to assume that the structure of alcohol is not greatly different whether it is liquid or solid. (5)

But for the verification of these supposition the author thinks it necessary to study some other properties.

Lauryl alcohol

Bernal (6) has reported from his X ray study the rotational transition of lauryl alcohol, but Otto (7) has not found any anomalies. By thermal analysis Phillips and Mumford (8) found the transition in the cooling curve, but not in the heating. Frosch (9) found the dielectric anomaly, which could not be detected by Hoffman and Smyth. (10)

Hoffman and Smyth purified the sample carefully, (its m. p. was 23.5°) and found the curve as shown in Fig. 9.

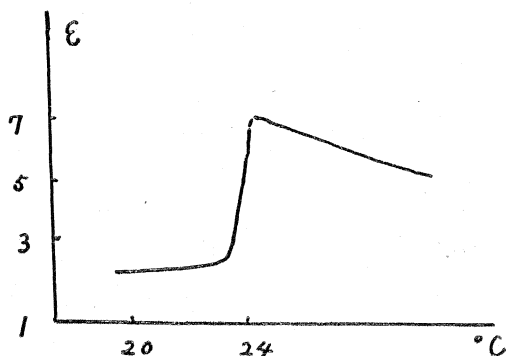


Fig. 9. Dielectric constant for pure sample (Hoffman and Smyth)

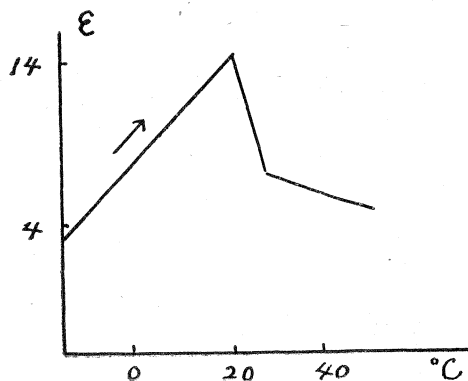


Fig. 10. Dielectric constant for impure sample (Hoffman and Smyth)

The curves at 0.5 K. C. and 5 K. C. coincide in cases of both heating and cooling. This shows there is no anomaly. Furthermore they have shown the result as Fig. 10 in case of impure sample, and explained the maximum of the curve as the result of the action of some impurities such as hydrate, and not as the result of transition of lauryl alcohol. And they supposed that Frosch was mistaken in conceiving the maximum due to hydrate as the transition phenomena. *

Hereupon the author measured the dielectric constant and electric conductivity in warming and cooling before he studied the effect of the electric field.

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

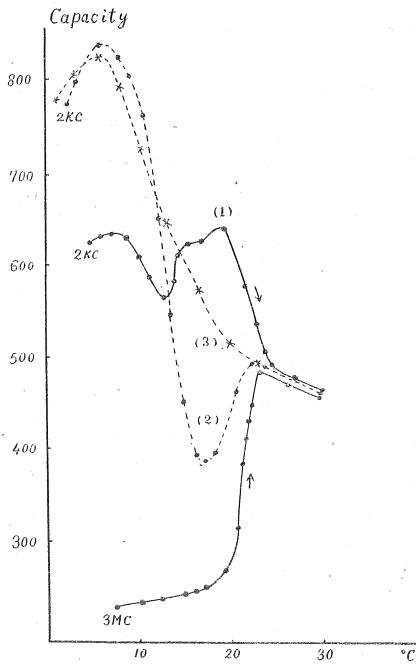


Fig. 11. D.C. and A.C. effect for the dielectric constant.

The sample was fractionated as cetyl alcohol. Its m.p. was $22.5^{\circ}-23^{\circ}$. *

In order to compare the impurity with that of prior investigators, the electric conductivities in liquid are shown as follows.

Hoffman and Smyth	17×10^{-10}
Frosch	42×10^{-10}
The author	$45-5 \times 10^{-10}$

The results of measurements were shown as in Fig. 11, Fig. 12 and Fig. 13.

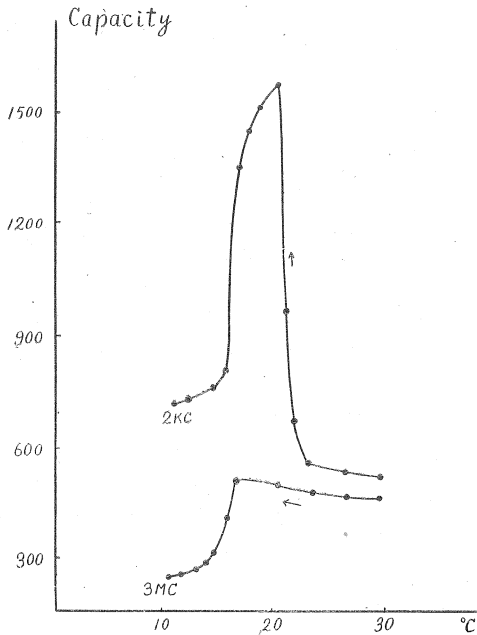


Fig. 12. Temperature dependence of the dielectric constant in the cooling process.

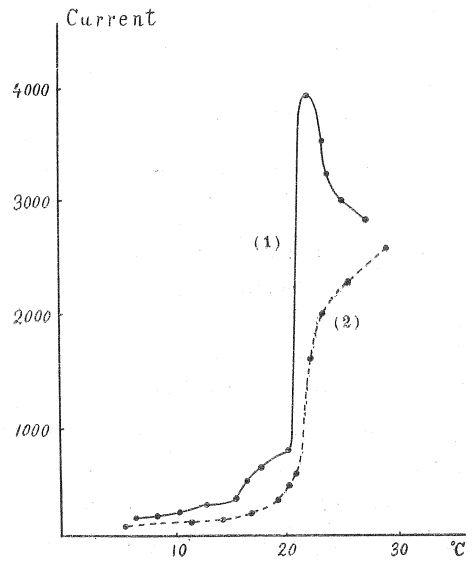


Fig. 13. D.C. effect for the electric conductivity.

* It was kindly offered by Prof. J. Noguchi

The transition phenomena can thus be clearly seen both in warming and cooling, but especially more so in cooling.

In Fig. 11 and Fig. 12 the curves by 2 K.C. and 3 M.C. do not coincide, and this fact shows that the sample of the author had the purity lower than of Hoffman and Smyth.

When the sample was solidified under a D.C. electric field, the results shown in the curve (2) in Fig. 11 and Fig. 13 were obtained. Fig. 11 shows the maximum of the right side disappeared by the D. C. electric field. By comparing with the case of cetyl alcohol, it can be assumed, therefore, that the maximum was due to the transition. From Fig. 13 the same thing can be assumed. Conversely the maximum of the left side in Fig. 11 did not disappear, but was somewhat elevated by the D. C. electric field. So it is supposed that the maximum will correspond to that of impure sample of Hoffman and Smyth. Therefore the transition seemed occur when the purity of the sample was between the purity and impurity of Hoffman and Smyth. It can be supposed that the transition point was lowered by a minute impurity and appeared before the melting.

Such a fact had already been found by Kakiuchi, Sakurai and Suzuki in the measurement of specific heat. (11)

When the sample was solidified under an A. C. electric field, the result was the curve (3) shown in Fig. 11, but the explanation for this cannot be given satisfactorily.

In the case of 3 M.C. measurements, no electric field effect in both D. C. and A. C. was found as in the case of cetyl alcohol.

Amilan

Amilan is a polymer as a Nylon which has hydrogen bonds. The sample was kindly offered by Toyo Rayon Co. Its m.p. was about 210°.

It was fitted between the electrodes of the condenser by melting it in vacuum to prevent oxidation. The dielectric constant curve was as (1) in Fig 14 or Fig. 15. When the sample was treated by D. C. electric field in the solid state (140°), its current

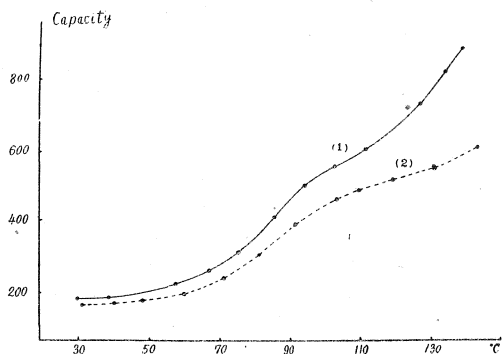


Fig. 14. D. C. effect for the dielectric constant (2 K. C.)

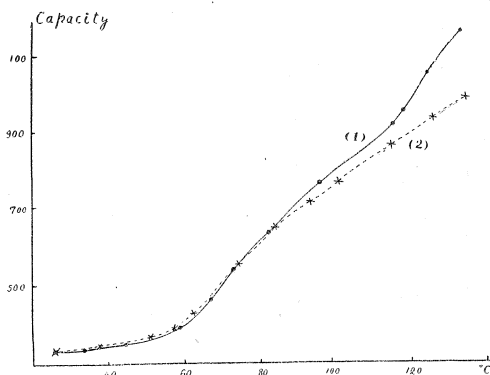


Fig. 15. A. C. effect for the dielectric constant (2 K.C.)

was about $200\mu\text{A}$, for 14 hours, and the result was as (2) in Fig. 14 showing a decrease of dielectric constant.

When the sample was treated by A.C. electric field in the solid state (140°), its current was about 0.7 mA, for 5 hours, and the result was as (2) in Fig. 15 showing also a decrease of dielectric constant. Although these treatments were made in vacuum some exdization and thermal decomposition might have taken place. But the cause of the electric effect seemed chiefly due to the decrease of hydrogen bonds.

In conclusion the author wishes to express his sincere thanks to Dr. Y. Kakiuchi and Professor H. Shyoji for their kind guidance. He also expresses his gratitude to Toyo Rayon Co. for the gifts of amilan, and to Mr. A. Tanaka and T. Koikeda for their cooperation.

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