On the Dielectrics treated by an Electric Field II

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On the Dielectrics treated by an Electric Field II.

By

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Introduction

In the previous paper[1] the author reported the fact that the dielectric constant of cetyl alcohol if solidified under a D. C. electric field or made to flow with D. C. current in solid state apparently decreased (D. C. effect), while the value of the same substance solidified under an A. C. electric field increased (A. C. effect). Since then some experiments have been made to find out the causes of these phenomena. The results given are far from conclusive, but the author wishes to make an intermediate report on some of them.

Besides, some reports of experimental results concerning palmitamide and pentaery-thritol which have hydrogen bonds are given below.

Cetyl alcohol

(1) Relations between A. C. effect and frequency.

A sample filled between the electrodes of a plate condenser, was heated above the melting point and then cooled to the room temperature under an alternating electric field supplied from a commutator and a D. C. electric source of 1000V. Fig. 1 (a). The oscillogram of the electric voltage was as shown in Fig. 1 (b), when the frequency was less than several times per second, but, as the frequency increased, the curve was considerably distorted owing to the defect of the brush contact of the commutator.

The results obtained by this procedure are as follows. When the frequency was several times per second, the A. C. effect was nearly invisible, but it increased with the frequency, reaching the saturation value with the frequency of 30 per second. Some examples are shown in Fig. 2.

Fig. 1. Commutator and oscillogram

In each case, the electric field was applied for 3 minutes in liquid and 12 minutes in solid, and the dielectric constant was measured by the low frequency bridge under the frequency of 2. K. C. per second as reported in the previous paper.[1]
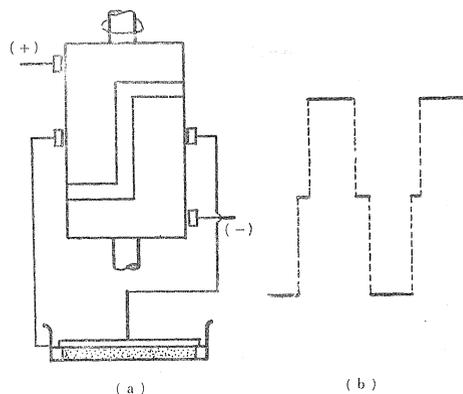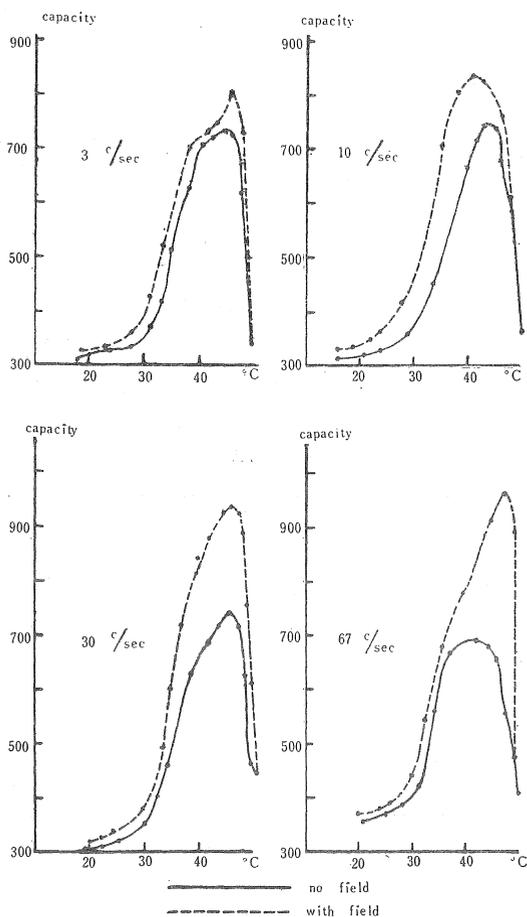
(2) Change of specific heat.

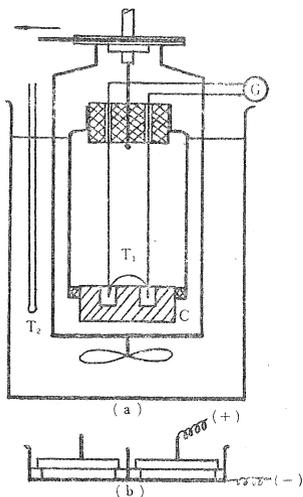Fig. 2.   Variation of A. C. effect with frequency

Fig .3   Apparatus

According to Smyth and his collaborators[2][3][4] the dielectric anomaly of normal solid alcohol was attributed to the rotation of molecules around their long axis in solid phase. Therefore it seemed useful to find out how the treatment by an electric field change the specific heat of alcohol. In the beginning several experimental procedures based on the principle of differential thermal analysis were attempted using the specimens themselves which had been treated by an electric field without powdering them, but no good reproducibility of the result could be obtained, but when the method of using powdered specimen was attempted the author succeeded in obtaining some reproducibility.

(Experimental apparatus)

The experimental apparatus is shown in Fig. 3. C is a copper block of 5 cm in diameter and 3 cm in thickness with two holes (diameter 1.6 cm, depth 2 cm) arranged symmetrically about the centre. In the one hole cetyl alcohol was filled, and, in the other, paraffin (m. p. about 55°), as the reference substance. T_1 is a thermo-junction of copper-constantan wires (0.5 mm in diameter). The sensitivity of the galvanometer was 3.3 cm deflection at 1m scale per degree. The water of the bath was heated by an electric heater, and the time rate of the temperature rise was about 1℃ per minute. Care was taken that the condition of the temperature rise should be the same all the time, and the conditions of the heat conduction to the two samples should be equal. For instance, two samples were equally powdered, and equal quantity was filled under equal conditions, and two junctions were set in the centre of the samples at the equal depth.

The method of the treatment of the sample by an electric field was as reported in the previous paper, and the vessel is shown in Fig. 3 (b). Two electrodes were nickel plated and insulated by three glass spacers (thickness : 1.4 mm), and two solid samples were torn off from the electrodes and each was powdered in the mortar.

The deflection of the galvanometer and the temperature of the water were observed. The relation between the temperature of the water and that of the sample had been previously marked.

(Experimental results)

Both commercial crude cetyl alcohol and the one which had been once fractionated at a reduced pressure were used. But as the difference between them was chiefly in their transition points and qualitatively they were nearly alike, commercial crude sample was mainly used. (1.9 gr at an experiment)

The results are as follows.

A result of the differential thermal analysis using paraffin and cetyl alcohol solidified under an A. C. electric field 1000V/1.4 mm is shown in Fig. 4 as one example. It seems that the two curves of both cases (with or no field) are approximately coincident, and that the heat of transition of both samples (with or no field) are nearly equal. The curve obtained by using cetyl alcohol solidified under a D. C. electric field also coincided approximately with the above curves. Therefore the heat of transition of cetyl alcohol seems also not to change in the treatment under a D. C. electric field.

Subsquently the differential thermal analysis using directly the two samples treated with electric field and no field instead of paraffin as the reference sample was attempted. The result of the case of using the sample solidified under A. C. electric field of 1000 V/1.4 mm is shown in Fig. 5 as one example. As shown in this, in most cases the maximum of the curve was found in the neighbourhood of the transition point.

In the case of using the sample treated under D. C. electric field a similar curve was also obtained.

Now, as the causes of showing such a maximum the following factors are supposed.

(1) the difference of the heat conductivity

(2) the difference of the heat of transition

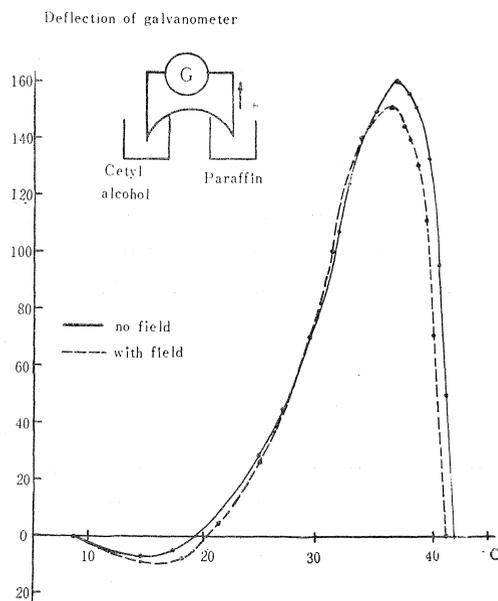(3) the difference of the transition point

But (1) would not be reasonable
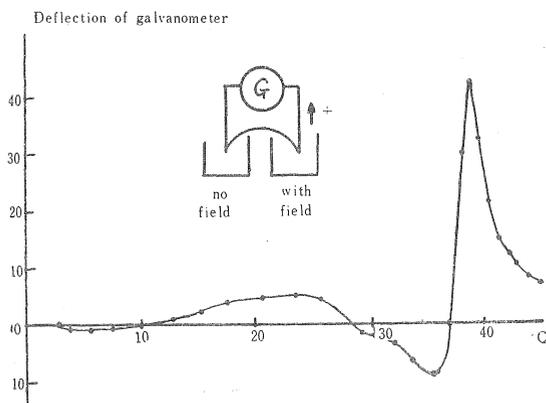

Fig. 4. Curves from the differential thermal analysis

Fig. 5.   Curves from the differential thermal
                analysis

considering the appearance of the minimum before the maximum, and (2) is unthinkable because of the sharpness of the maximum and the fact shown in Fig. 4. Eventually a small difference of the transition point will be the cause.

Accordingly, if the treatment by an electric field does not change the value of the heat of transition, it must be concluded that the treatment will not change the magnitude of molecular rotation. In order to explain the effect of treatment by an electric field upon the dielectric constant some other causes than the molecular rotation must be considered.

In relation to the explanation the following suggestions studied recently by other authors[5][6] must be refered. According to Kremmlings' opinion α–β_2 transition of cetyl alcohol will prohibit not the molecular rotation but only proton transfer. On the other hand Kojima and Ogawa concieved the proton magnetic resonance absorption which could be attributed to the molecular rotation in the β_2 phase. But it has not yet been concluded whether the apparent change of dielectric constant by the treatment under an electric field is a volume effect or a surface effect due to space charges near the electrodes.

(3)   Other experiment

In order to confirm whether molecular rotation alone is the cause of the effect of treatment by an electric field upon the dielectricc onstant, n–hexadecylpalmitate was studied. The substance is known to have no hydrogen bonds in solid but to have the molecular rotation.[7] As a result neither the D. C. nor A. C. effect could be found. It seems, therefore, that the principal factor causing the effect of treatment under an electric field is the proton transfer due to the hydrogen bonds as well as the molecular rotation.

Palmitamide

Anomalous dielectric constant and electric conductivity of palmitamide have been already attributed to the large mobility of protons forming hydrogen bonds by Kakiuchi[8] and Sakurai.[9] The present author made therefore, an experiment to see whether the treatment by an electric field upon palmitamide would give an effect like cetyl alcohol and amilan.[1] The method of the experiment was as shown in the previous paper.* The result is shown in Fig. 6. Curve (1) is for a sample solidified

*   The sample was kindly offered by Dr. Kakiuchi.

without electric field, (2) and (3) correspond respectively to the case where D. C. current of 1200 μ A under 75° was made to flow for 5 hours or two more hours. The effect was quite similar to that of amilan reported in the previous paper[1] and the causes will similarly be attributed to the decrease of hydrogen bonds due to the proton transfer.

On the other hand, for the verification of the proton conduction through palmitamide the simple method shown in the previous paper[10] was attempted. When D. C. current of some 3000 μ A at 85° was made to flow for one hour and a half the evolved hydrogen could be detectet, but not when A. C. current was used. These properties are similar to those of resorcin reported in the previous paper.[10]
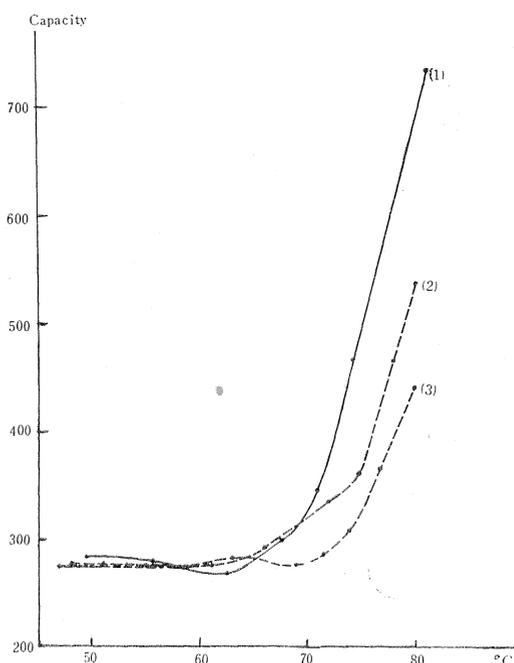

Fig. 6.   D.C. effect for the dielectric constant (2 K. C.)

Pentaerythritol

Recently Kiriyama and his coworkers[11] studied dielectrically pentaerythritol and found its anomaly attributed to its proton transfer. Because of the considerably rapid decomposition as well as sublimation near the melting point, the effect of the treatment by an electric field could not be confirmed, but the proton transfer was easily verified by the above mentioned method.* The evolved hydrogen could be detected when D. C. current of some 4 mA at 188° was made to flow for half an hour, and also in the case of A. C. current when a current of some 3 mA at 188° was made to flow for 40 minutes. These properties are similar to those of amilan reported in the previous paper.[10]

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*The sample was kindly offered by Dr. Nitta.

M. IDA

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