# Dielectric Anomaly of n-Higher Alcohols Solidified under an Alternating Electric Field


| メタデータ | 言語: eng<br>出版者:<br>公開日: 2017-10-03<br>キーワード (Ja):<br>キーワード (En):<br>作成者: Ida, Mitsuo, 井田, 光雄<br>メールアドレス:<br>所属: |
| --- | --- |
| URL | https://doi.org/10.24517/00011454 |

This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 3.0 International License.

The Science Reports of the Kanazawa University, Vol. VI, No. 1, 25—31, April, 1958

# Dielectric Anomaly of *n*-Higher Alcohols Solidified under an Alternating Electric Field

By

Mitsuo IDA

(Received Sep. 4, 1957)

The cause of the phenomenon found by the author, that the dielectric constants of *n*-higher alcohols increase if they are solidified under an alternating electric field was examined, and was attributed to the decrease of resistances to the rotation of dipoles.

## 1. Introduction

Previously[1][2] the author discovered the phenomenon that the dielectric constants of cetyl alcohol and $\alpha$-monostearin increase if they are solidified under an alternating electric field, and called this phenomenon the A. C. effect. And he tentatively attributed this effect to the increase of the number of hydrogen bonds in the substances. Since then some experiments were made to confirm this hypothesis. First he obtained Cole-Cole diagrams, and subsequently examined the effect of impurities upon the A. C. effect by putting some foreign substances into pure cetyl alcohol. Furthermore he examined the infra-red spectrum to detect the change of the number of hydrogen bonds of cetyl alcohol occurring upon solidification under an alternating electric field. Then the author found that the hypothesis stated above should be changed. The results of these experiments are described below.

## 2. Experimental procedure and results

(1) *Cole-Cole diagram*

The relation of the real part $\varepsilon'$ and the negative imaginary part $\varepsilon''$ of the complex dielectric constant of cetyl alcohol solidified under an alternating electric field was found by the procedure as was done in the previous paper.[3] The specimen used was the same which was used in that case, and contained some impurities. A typical example of the results obtained is shown in Fig. 1, where curve (1) is for a specimen solidified without an electric field, and curve (2) for one solidified under an alternating (60 c/s) electric field of 8.2 KV/cm. As the plotted curves nearly coincided with circular arcs, they were presumed to be circular arcs and their centers $0_1$, $0_2$ were obtained.

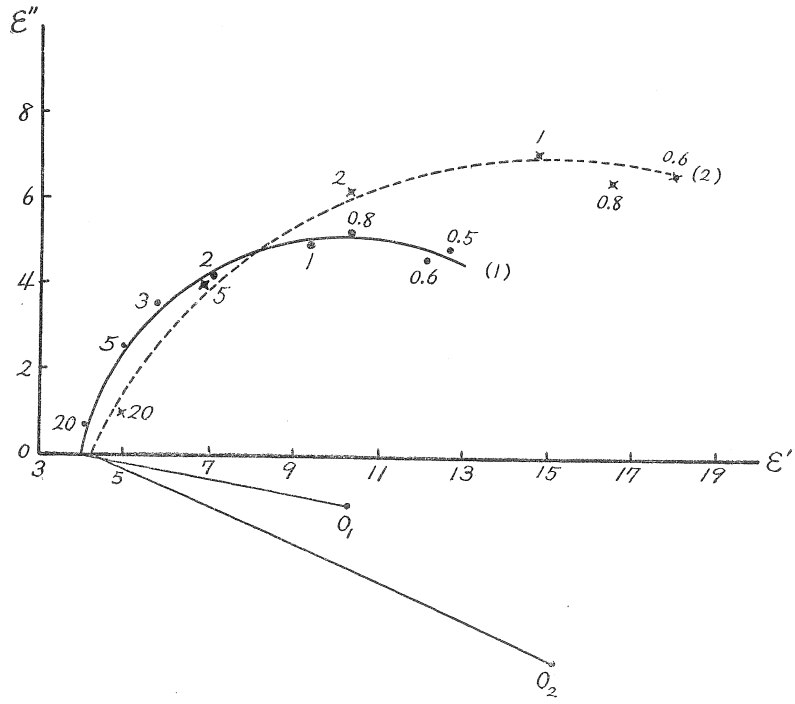


Fig. 1. Cole-Cole diagram at 45°C in the heating stage (cetyl alcohol). Numbers beside the plotted points indicate the frequencies in Kc/s. The points $0_1$, $0_2$ indicate the centres of curvature of the plotted curves (1) and (2) respectively.

From each diagram it can be easily recognized that the centre of each circle is located below the $\varepsilon'$ axis. And so we can say that the dielectric anomaly of cetyl alcohol in each case ought to be attributed to orientational polarization and not to a surface effect such as electrode polarization.[4]

(2) *The effect of impurity upon the A. C. effect*

The specimen of cetyl alcohol used in the previous experiment[1] contained some impurities. Then to investigate the effect of impurities upon the A. C. effect, the same experiments were carried out with a pure specimen ($S_0$) from the Eastman Kodak Co. (mp 48.7°C) and also with impure specimen prepared by adding 6.4% of octadecyl alcohol ($S_1$), tetradecyl alcohol ($S_2$), etc. to the pure substance mentioned above. A typical example of the results obtained is shown in Fig. 2.

Curve (1) shows the temperature dependency of the dielectric constant of pure cetyl alcohol $S_0$ solidified without an alternating electric field, the measurement being made at 2Kc/s in the heating stage. The maximum of the curve corresponds to $\varepsilon'=47$. Such a large value of dielectric constant, the author believes, has never been reported before. Perhaps this may be attributed to the extra high purity of the specimen, because if the specimen is mixed with any impurity the maximum of the curve always decreases as is reported below.

Curve (2) is for the pure cetyl alcohol $S_0$ solidified under an alternating (60 c/s)

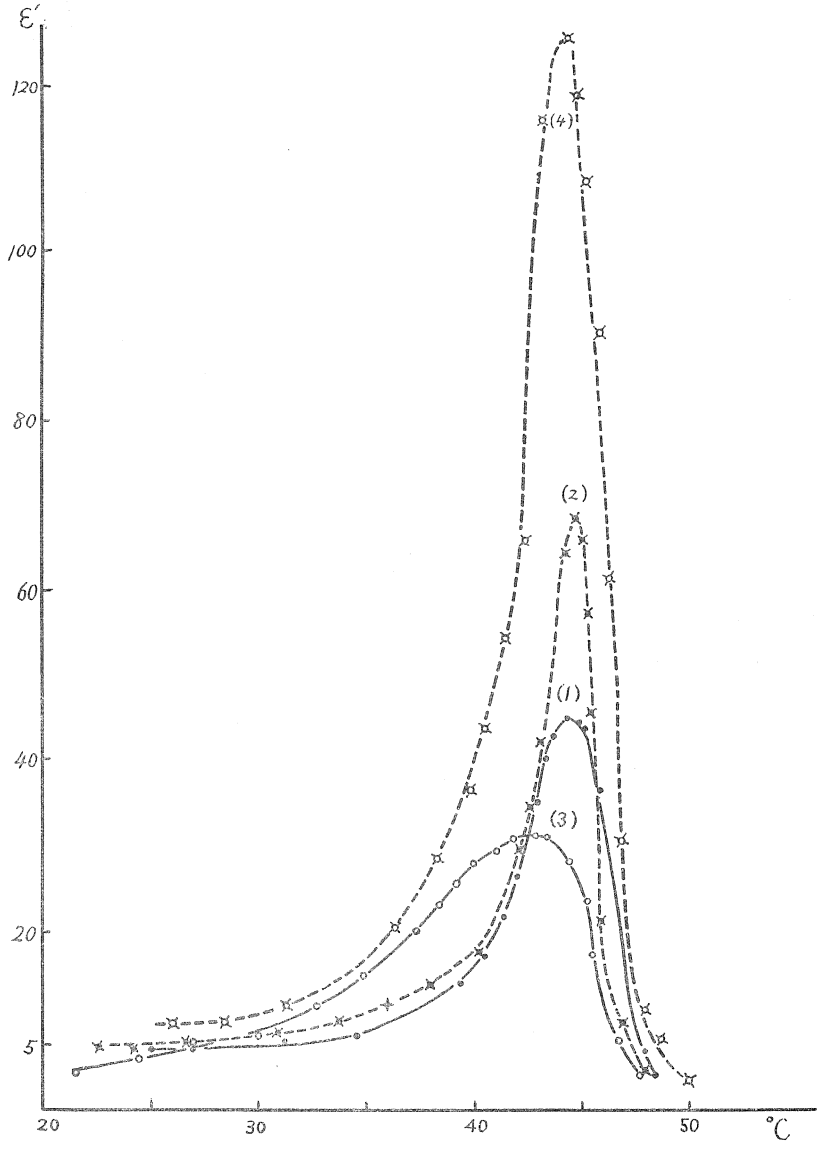


Fig. 2. Temperature dependency of dielectric constant of pure and impure cetyl alcohol (2Kc/s)

(1) pure specimen $S_0$
(2) A.C. effect of the pure specimen $S_0$
(3) impure specimen ($S_1$) containing 6.4% of octadecyl alcohol
(4) A.C. effect of the impure specimen $S_1$

electric field of 8.2 KV/cm, and its maximum corresponds to $\varepsilon'=69$. Thus the A.C. effect is shown also by the pure cetyl alcohol $S_0$.

Curve (3) is for impure cetyl alcohol $S_1$ containing 6.4% of octadecyl alcohol. It has also a lower peak than the curve (1) of pure cetyl alcohol as was stated above and is broader. But this specimen $S_1$ shows A.C. effect remarkably greater than the

pure one as shown in curve (4). Its maximum corresponds to $\varepsilon'=127$. When measured at the frequency of 600 c/s it reached even to $\varepsilon'=166$.

It was also examined that when a specimen of cetyl alcohol showing the A. C. effect as in curve (2) or (4) is melted, and then solidified, the A. C. effect of each vanishes in contrast with the preceding study.[1]

It was found that, when tetradecyl alcohol is used instead of octadecyl alcohol as the impurity, the concentration still being 6.4%, this comosite $S_2$ gives an $\varepsilon'$-temperature curve nearly similar given by the composite with octadecyl alcohol. The maximum of the curve is of course lower than that of the pure one. The A. C. effect is also more marked than that of the pure one but a little smaller than that of octadecyl alcohol composite. And this composite $S_2$ has also the property of losing the A. C. effect by the process of remelting.

From the results of these experiments with composites with octadecyl or tetradecyl alcohol it was found that with a higher concentration, the A. C. effect becomes smaller and the concentration of about 6.4% seems to give the maximum A. C. effect.

The composite of pure cetyl alcohol with 6.4% stearic acid, ethyl stearate, or paraffin also gave nearly similar $\varepsilon'$-temperature curves, and their maxima are lower than that of the pure specimen. The A. C. effect was also present, but it was not so large as in the composites with alcohols, rather a little smaller than that of pure one as is shown in Fig. 3. The A. C. effect did not survive by the process of remelting in these composites as in the former composites of alcohols.

That is in these composites the state attained by solidification under an alternating electric field did not remain after they were remelted. But in the case of the one containing 23% of stearic acid plus 5% of tetradecyl alcohol and in the fairly imure

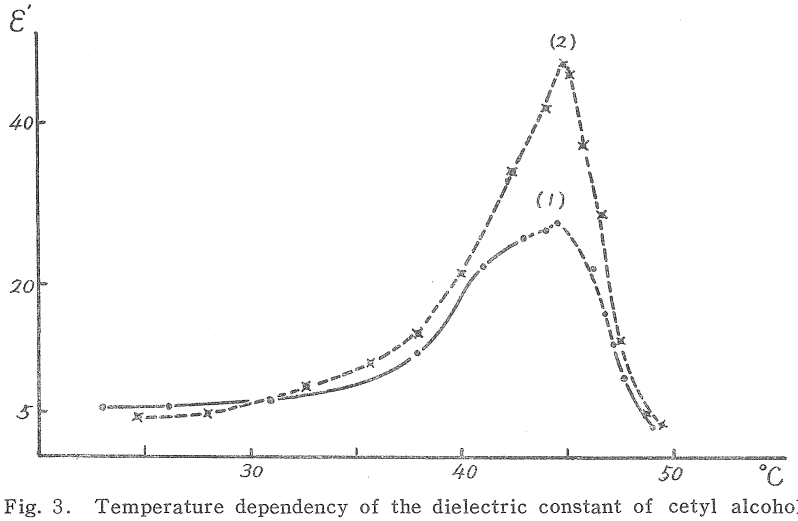


Fig. 3. Temperature dependency of the dielectric constant of cetyl alcohol $S_3$ containing 6.4% of ethyl stearate (2Kc/s)
(1) Without an alternating electric field
(2) A. C. effect

specimen containing several substances as stearic acid, tetradecyl alcohol, and paraffin, the state attained by solidification under an alternating electric field did not completely disappear, but a fair amount of it remained.

(3) *Infra-red study*

As was mentioned above we found that the A. C. effect occurred both in pure and impure cetyl alcohol. And in the previous paper [1] the author supposed that the A. C. effect was tentatively attributed to the increase of the number of hydrogen bonds in the substance. But in the present experiment we found that the A. C. effect of the composite containing other alcohols is more remarkable than that of the pure substance. So it became necessary to reexamine the previous supposition, because the number of hydrogen bonds generally decreases as the amount of impurities increases. So even if the number of hydrogen bonds increases by an alternating electric field it is unreasonable to suppose the increase of the number of hydrogen bonds to be larger in the impure specimen than in the pure. And the explanation of the A. C. effect by the increase of the number of hydrogen bonds became doubtful. So the author attempted to ascertain by infra-red spectroscopy whether the number of hydrogen bonds changed when the A. C. effect appeared.

Now, for infra-red study of a specimen in the solid state a thin film of it must be prepared, and so a specimen must be once melted and then the liquid film be solidified. Therefore if the state of the specimen is changed by melting this will also happen in infra-red study. But as was reported in the case of impure cetyl alcohol, the state attained by solidification under an alternating electric field remains almost intact.[1] That is, the A. C. effect of this specimen almost wholly remains, although it had been melted and solidified.

So the same specimen of impure cetyl alcohol used in the previous paper[1] had to be used in the present study although it was desirable to use the pure specimen. The specimen was solidified under an alternating electric field, and a small quantity of it was heated to melting on a silica glass plate (thickness 0.9 mm) and a warmed cover glass (thickness 0.15 mm) was pressed on it, and cooled down to the room temperature.

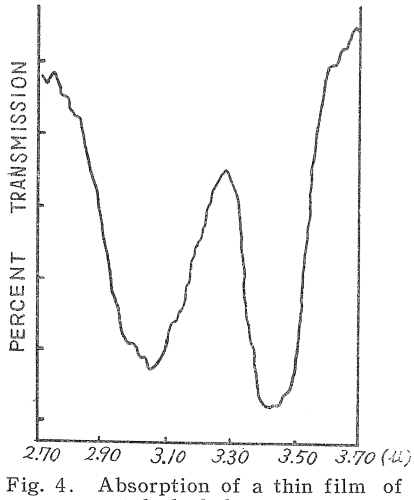

Fig. 4. Absorption of a thin film of cetyl alcohol.

A spectrometer equipped with a sodium chloride prism was used. The infra-red transmission curve obtained is shown in Fig. 4. In this curve the maxima of absorption are situated at 3.05 $\mu$ and 3.43 $\mu$. These correspond to OH and CH vibrations respectively. The aspect of this curve, especially the maximum point of absorption, are similar to the curve obtained by Davies[5] with a quartz prism.

When the specimen solidified without an electric field was also examined in the same manner the curve obtained almost completely coincided with that shown in Fig. 4. And hardly any difference can be seen between the curves of the specimens solidified with and without an alternating electric field. Therefore it is to be concluded that hardly any change of the number of hydrogen bonds occurred although the specimen was solidified in an alternating electric field.

## 3. Discussion

In the previous paper [3] the author concluded that the dielectric anomaly of n-higher alcohols in the "Waxy state" is to be attributed to the orientational polarization, and in this paper he showed that the dielectric anomaly of cetyl alcohol solidified under an alternating electric field is also to be attributed to the same cause. Then the cause of the A. C. effect must be either increase of the number of hydrogen bonds or decrease of the resistances to the rotation of dipoles. In the previous paper[1] the author assumed the former alternative, referring to the Pauling's consideration.[6] But now he found experimentally that the change of the number of hydrogen bonds does not happen, though the specimen shows A. C. effect, and also that the A. C. effect of pure specimen vanishes by remelting and solidification.

So he now concluded that the cause of the A. C. effect must be attributed to the decrease of the resistances to the rotation of dipoles. And this is not unreasonable. Because we can easily imagine that when cetyl alcohol is solidified under an alternating electric field, the substance crystalizes while its molecules are in a state of vigorous rotational oscillation, and the resistance to the rotation of dipole decreases after the solidification. Then the dipole of the molecule can easily oscillate when the measuring alternating electric field is applied. That is, the value of $\varepsilon'$ increases and the A. C. effect appears.

And the reason why the composites containing octadecyl alcohol or tetradecyl alcohol show a larger A. C. effect, can also be explained by assuming that in these composites the molecules of two kinds form crystalize more loose than in the pure specimen and are in the state capable of rotation with lesser resistance. The A. C. effect of the composites with the substances other than alcohols is not so large probably because in these composites the resistance to the rotation of dipoles does not decrease so much.

## 4. Acknowledgement

The author wishes to express his sincere thanks to Professor T. Fujiwara of Hiroshima University for his kind advice and suggestion. His acknowledgement is also due to Professor H. Shoji for the encouragement throughout the work. The author's thanks are also due to Mr. F. Asai for his help in the study of infra-red spectra and to Mr. M. Takeyama of Hiroshima University for his kindness in supplying the specimens.

## References

[1] M. Ida : Sci. Rep. Kanazawa Univ. **2** (1954) 23.

[2] M. Ida : Ibid, **4** (1955) 35.

[3] M. Ida : Ibid, **5** (1956) 7.

[4] J. E. Johnson and R. H. Cole : J. A. C. S. **73** (1951) 4536.

[5] M. M. Davies : J. C. P. **8** (1940) 577.

[6] Pauling : The nature of the chemical bond (1948) 308.