*Dielectric Properties of Starch. II. High Frequency Loss Process**

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In Part I$^{1)}$ of this series the dielectric properties of starch at audio frequency region were discussed. In the present paper, dielectric measurements have been made on the α- and β-modification of potato starch containing various amounts of water in the frequency range from 2kc. to 3mc. Dielectric dispersion, which was called "high frequency loss process" in Part I, was again observed and has been discussed.

Experimental

Dielectric constant, ε', and loss factor, ε'', were measured in the frequency range from 2 to 30 kc. using the Schering bridge described in the previous paper$^{1)}$, and the radio frequency range from 190 to 3000 kc. was covered by Heathkit Model QM-1 Q-Meter which is shown in Fig. 1. Mica condenser, C_m, having practically pure capacitance of about 5000 $\mu\mu F$, was connected in series with the dielectric cell between the terminals T and T′ in order to make the vacuum tube voltmeter circuit operate normally even when the cell had an appreciable loss. The loss tangent, $\tan\delta$, and the capacitance, C_x, of the dielectric cell are readily calculated from

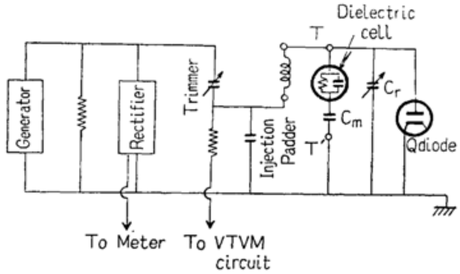

Fig 1. Circuit-diagram of Heathkit Model QM-1 Q-Meter.

$$\tan\delta = \frac{A+2}{A+1}\,\frac{C_1(Q_1-Q_2)}{(C_1-C_2)Q_1Q_2}$$

$$C_x = \frac{C_m(C_1-C_2)}{C_m-(C_1-C_2)}$$

$$A = C_m/C_x$$

where C_1 and Q_1 are the value of resonance condenser C_r and the Q value of the circuit, respectively, observed at resonance without the dielectric cell. C_2 and Q_2 are the values observed at resonance with the dielectric cell.

Other experimental procedures were the same as those described in Part I.

Results

The variations of ε' and ε'' with temperature for the β-modification cotaining various amounts of sorbed water at 700 kc. or its neighborhood are shown in Fig. 2. The curve v in this figure represents the one for the starch which was dried for 12 hr. at 80°C under the reduced pressure of 7 mmHg. It can be seen from Fig. 2 that ε'' of each sample has its maximum value $\varepsilon''_{\max}$, although the shape of the curve is so flat that the temperature T_m where ε'' passes through a maximum is not determined accurately. The temperature coefficient of ε' of each sample is always positive and seems somewhat greater at the temperature near T_m. An increase in sorbed water produces serious variations in the data; ε' increases as has been observed previously$^{1)}$, $\varepsilon''_{\max}$ value increases, and T_m shifts to lower temperatures. The lower values of ε' and $\varepsilon''_{\max}$ for the sample of 17.5% water content seem to be mostly due to its smaller

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1) S. Ono, T. Kuge and N. Koizumi, This Bulletin, **31**, 34 (1958).

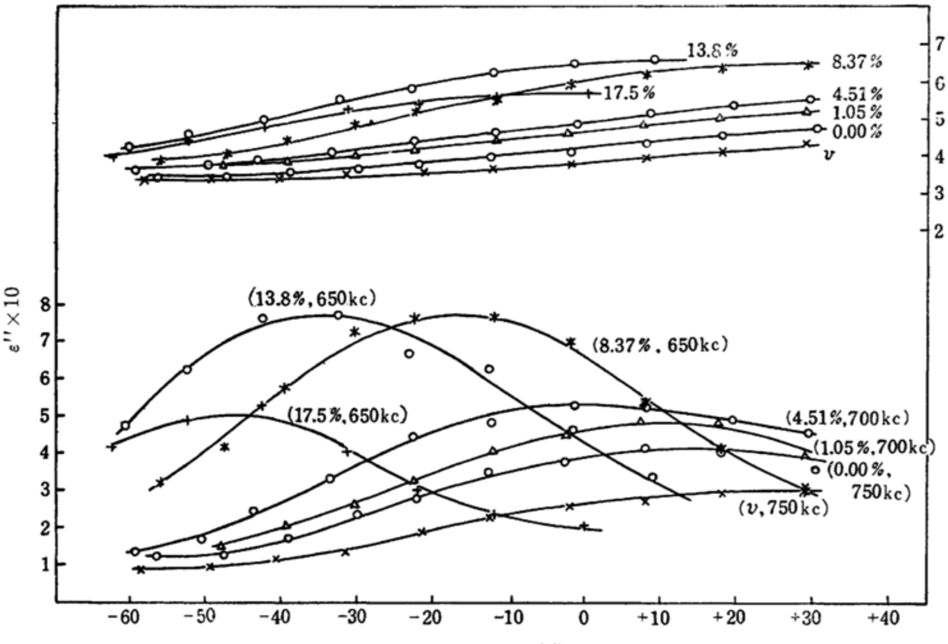

Fig. 2. Temperature dependence of ε' and ε'' of β-modifications of potato starch containing sorbed water at the inscribed amounts (g./100 g. dry starch) and frequencies.

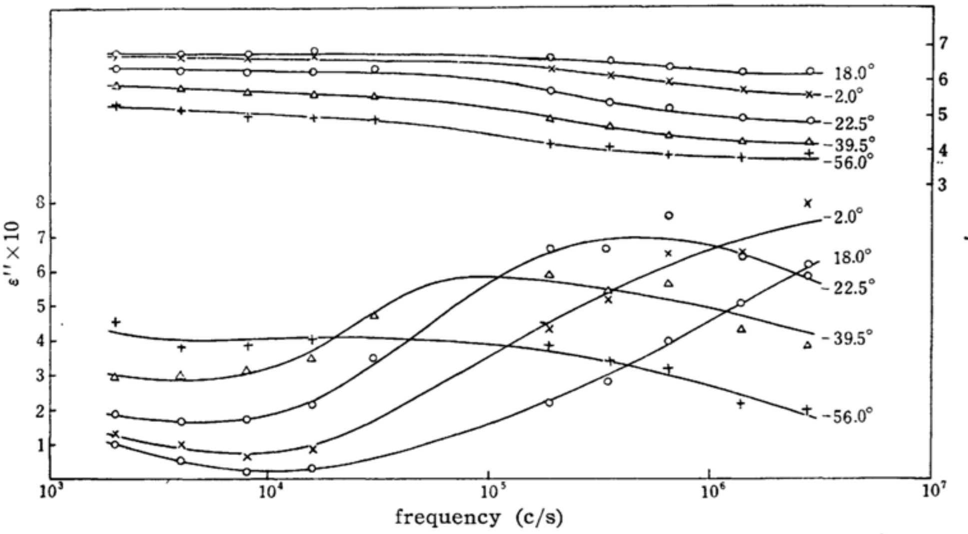

Fig. 3. Frequency dependence of ε' and ε'' of β-modification of potato starch containing 8.37% water (g./100 g. dry starch) at several different temperatures.

volume fraction of starch than that of those of the other samples.

At a given water content, ε' and ε'' are affected remarkably by the frequency and the temperature of measurement. Figs. 3 and 4 show the typical frequency dependences of ε' and ε'' for both modifications. The critical frequency f_m where $\varepsilon''_{\max}$ occurs shifts to lower frequencies as the temperature is lowered. The relation between f_m and the temperature for each sample is given in Fig. 5. It can be seen that a plot of $\log f_m$ against reciprocal absolute temperature is almost a straight line. Since the data at frequencies 30—190 kc. are lacking in our study, a considerable number of errors might be encountered when the figures showing the frequency dependence of ε'' at a given temperature, e.g. Figs. 3 and 4, were used

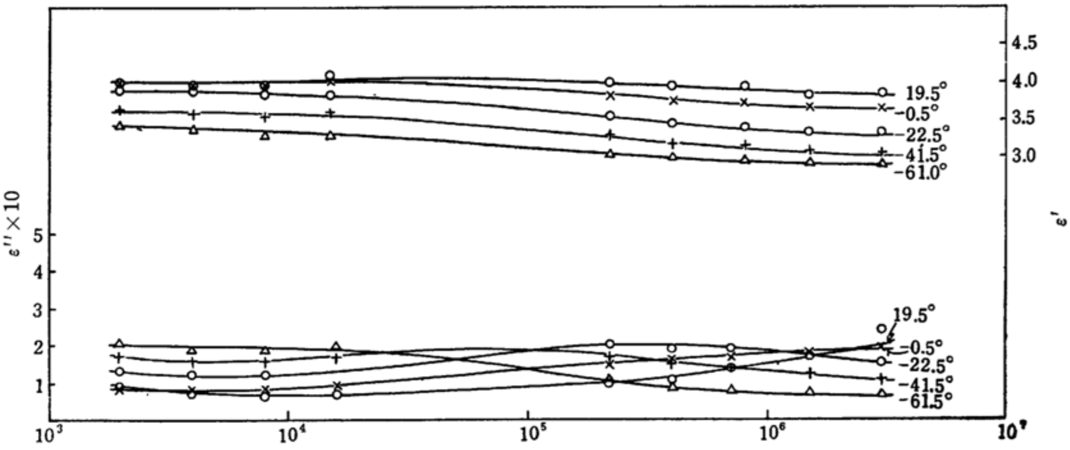

Fig. 4. Frequency dependence of ε' and ε'' of α-modification of potato starch containing 8.84% water (g./100 g. dry starch) at several different temperatures.

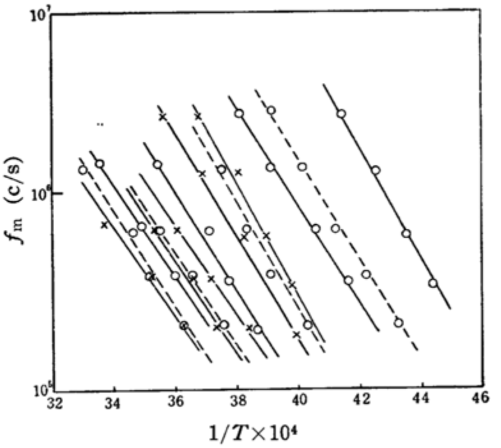

Fig. 5. Relation between critical frequency and temperature for potato starch which contain sorbed water at the inscribed amounts (g./100 g. dry starch).
—— β-modification ---- α-modification

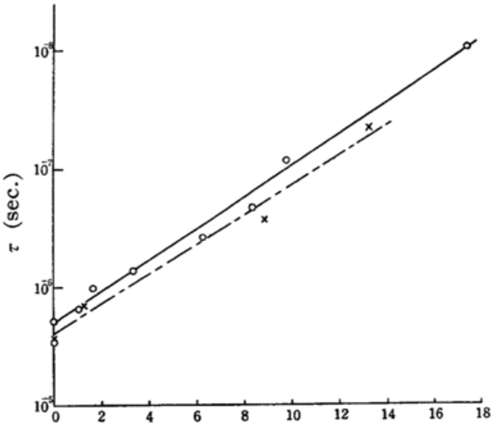

Fig. 6. Relation between the mean relaxation time and water content of potato starch at −15°C.
—○——○— β-modification
-×- - -×- α-modification

in determining the critical frequency. Therefore, T_m was taken at a given frequency from the figures which show the temperature dependence of ε'', e.g. Fig. 2, and now this frequency was regarded as the critical frequency at the temperature T_m. The relation given in Fig. 5 was thus obtained.

The mean relaxation time, $\bar{\tau}$, of the dielectric loss process may be regarded as

$$\bar{\tau}=1/2\pi f_m \tag{1}$$

The values of $\bar{\tau}$ calculated from f_m which was obtained by interpolation or extrapolation to −15°C in Fig. 5 are listed in Table I. When the log $\bar{\tau}$ is plotted against the water content, an almost linear relationship is found in the range examined. (Fig. 6)

By the use of the theory of absolute reaction rate developed by Eyring et al.[2], the relaxation time can be expressed by

$$\frac{1}{\bar{\tau}}=\frac{\boldsymbol{k}T}{\boldsymbol{h}}\exp(-\Delta F^{\neq}/\boldsymbol{R}T) \tag{2}$$

where $\boldsymbol{k}$ and $\boldsymbol{h}$ are Boltzmann's and Planck's constant, respectively, and $\Delta F^{\neq}$ is the free energy of activation for dielectric relaxation. This can be rewritten as

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[2] S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rats Processes", McGraw Hill Book Co. Inc., New York (1941), p. 548.

TABLE I

VARIATIONS OF THE THERMODYNAMIC QUANTITIES AND RELAXATION TIME WITH CHANGE IN WATER CONTENT

modification	water content g./100 g. dry starch	$\Delta F^{\neq}$ at $-15°C$ kcal./mole	$\Delta H^{\neq}$ kcal./mole.	$\Delta S^{\neq}$ at $-15°C$ e.u.	$\bar{\tau}$ at $-15°C$ sec.
β	0.00(v)*	8.48	9.80	9.77	2.84×10^{-6}
	0.00	8.27	10·6	10.6	1.87×10^{-6}
	1.05	8.15	10.9	11.0	1.59×10^{-6}
	1.62	7.95	10.3	11.6	1.00×10^{-6}
	3.35	7.78	11.3	12.5	7.24×10^{-7}
	6.24	7.47	11.8	13.7	3.89×10^{-7}
	8.37	6.91	11.9	15.9	2.15×10^{-7}
	9.80	6.67	11.5	16.8	8.40×10^{-8}
	17.5	5.57	12.6	21.0	1.00×10^{-8}
α	0.00	8.45	10.9	9.90	2.69×10^{-6}
	1.16	8.14	10.9	11.1	1.45×10^{-6}
	8.84	7.28	12.2	14.4	2.75×10^{-7}
	13.3	6.38	11.5	17.9	4.55×10^{-8}

* v represents the sample dried under the pressure of 7 mm Hg for 12 hr. at 80°C.

$$\frac{1}{\tau}=\frac{kT}{h}\exp(-\Delta H^{\neq}/RT)\exp(\Delta S^{\neq}/R) \tag{3}$$

where $\Delta H^{\neq}$ is the heat of activation and $\Delta S^{\neq}$ is the entropy of activation for dielectric relaxation. From Eqs. (1) and (3)

$$-\Delta H^{\neq}=\frac{R\,\mathrm{d}\ln f_m}{\mathrm{d}(1/T)}+RT \tag{4}$$

Therefore, $\Delta H^{\neq}$ can be obtained from the slope of the curve drawn in Fig. 5. $\Delta S^{\neq}$ may be calculated since $\Delta F^{\neq}$ is now known. These values are presented in Table I.

In considering those quantities as a function of water content, we should take those values at a particular temperature, since they are also functions of temperature. It is seen in appearance that $\Delta H^{\neq}$ increases with increasing water content. However, it may be reasonable to think that all $\Delta H^{\neq}$ would take the similar value of about 11 kcal./mole as a mean, because the errors for the determination of f_m would be appreciable, for the absorption maximum is flat, and the values of $\Delta H^{\neq}$ given in Table I are not ones obtained at a particular temperature. Eleven kcal./mole was used as the value of $\Delta H^{\neq}$ in the calculation of $\Delta S^{\neq}$ for all samples.

Discussion

There are two main theories which have been advanced to account for the dielectric relaxation process. One is the dipolar theory first proposed by Debye, in which the relaxation time of the absorption process depends on the hindrance to free rotation imposed on the dipolar group by the environment, and the other is the inhomogeneity theory proposed by Maxwell and Wagner, in which the relaxation time is governed by the relative dielectric constant and the conductivity values attached to the constituents of the material. Both give similar dependence of the dielectric constant and loss factor on frequency and temperature, so that it is impossible to determine which mechanism is responsible for the process by means of the analysis of the phenomena.

According to the consideration by Sillars[3], the water, which is considered to be present as single molecule or in a small group of molecules throughout the starch granule[4], may not produce serious loss due to Maxwell-Wagner type.

In the previous paper[1] we considered that Maxwell-Wagner type effect would occur in the low frequency loss process. The dielectric dispersion described in this paper, which has been called the high frequency loss process in Part I, may be attributed to the hindered rotation of hydroxyl group from the following reasons. i) The absorption curves for the carbohydrates, such as glucose[5], maltose[5], cellulose[6,7] and starch, are very similar to

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[3] R. W. Sillars, *J. Inst. Elect. Eng.*, **80**, 378 (1937).

[4] N. N. Hellman and E. H. Melvin, *J. Am. Chem. Soc.*, **72**, 5186 (1950); N. N. Hellman, T. F. Boech and E. H. Melvin, ibid., **74**, 348 (1952).

[5] P. Abadie, R. Charbonnière, A. Gidel, A. Girard and A. Guilbot, *J. chim. phys.*, **50**. C46 (1953).

[6] L. Pungs, *Electrotech. Z.*, **A75**, 433 (1954).

[7] R. Seidman and S. G. Mason, *Can. J. Chem.*, **32**, 744 (1954).

each other in respect to the fact that the curve has a very broad maximum in the frequency region of a few to ten megacycles at room temperature. That is, these loss processes have the relaxation time and its distribution of the same order. ii) The value of $\Delta H^{\neq}$ obtained for starch can be compared with those for cellulose (11.7 kcal., for 3.3% water content)7), ice (13.3 kcal.)8) and the hydroxyl group of terylene (12.4 kcal.)9).

Since the hydroxyl groups of starch and/or the sorbed water cause the high frequency loss process, we should take into consideration the situation of the hydroxyl group in the micell of starch. The effect of the sorbed water on the dielctric relaxation should be considered from the change of the micellar structure due to water penetration into the granule. Considering the large swelling of the starch granule by the sorption of water4), it is certain that the sorbed water loosens the forces between the starch chains, thus facilitating the movements of the hydroxyl group of the starch. In the previous paper1), the change of polarization of starch has also been interpreted by the loosening effects of water on the micell structure. An increased moment which orientates to the electric field can result from the water sorption, because the greater part of the sorbed water may be considered to be combined with the hydroxyl group of starch and to rotate together with it. From the above considerations, experimental results that $\Delta F^{\neq}$ decreased, $\bar{\tau}$ became shorter and $\varepsilon''_{\max}$ increased with increasing sorbed water, are now understood well.

Abadie et al.5) concluded from the variation of the critical frequency with increasing water content that the water, below a 15—16% water content, was believed to be bound chemically, while the water, above this limit, appeared to be adsorbed physically*. Our results, however, show that such a distinction can not be made, since $\bar{\tau}$ decreases continuously with the sorbed water, as can be seen in Fig. 6.

Comparing the values of $\bar{\tau}$, $\Delta H^{\neq}$, $\Delta F^{\neq}$ and $\Delta S^{\neq}$ of the α-modification with those of the β-modification, we can find no significant difference between them when the accuracy of the estimation of f_m is allowed for, though $\bar{\tau}$ of both modifications lies on the separate two lines in Fig. 6 respectively.

The most interesting feature is the fact that the value of $\varepsilon''_{\max}$ increases with increasing temperature as is seen in Fig. 3. This is unusual in the Debye type absorption. We have analyzed the data by the Cole-Cole plot method10). Fig. 7 shows one of these plots indicatig greater value of $\varepsilon''_{\max}$ for higher temperature. It can also be seen that the static dielectric constant, ε_s increases with increasing temperature and that the parameter α, a measure of the distribution of the relaxation times, is almost independent of temperature. Neither the value of α appreciably varied with water content in our study. The small variation of the optical dielectric constant, ε_∞, with temperature which is seen in Fig. 7 is most likely owing to the increase in the density of the liquid paraffin between the electrodes so that ε_∞ seems to be independent of temperature.

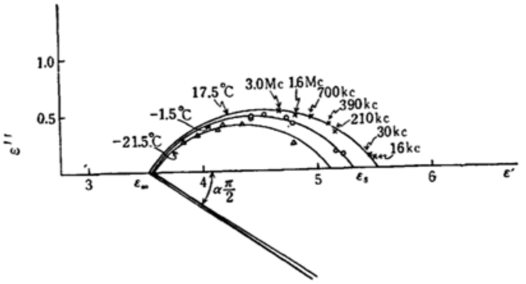

Fig. 7. Cole-Cole plot of the β-modification of starch containing 1.62% water (g./100 g. dry starch).

According to Fröhlich11), for temperatures below the transition point, increased temperature creates some disordered arrangement of dipole in crystalline solid, thus leading to increase in ε_s, which can be expressed as

$$\varepsilon_s-\varepsilon_\infty \propto \exp(-V/kT) \text{ when } V \gg kT \quad (5)$$

where V is the energy difference of a dipole in the two equilibrium directions. If the distribution of relaxation times is independent of temperature, it follows that

$$\varepsilon''_{\max} \propto \exp(-V/kT) \quad (6)$$

Although quantitative treatment is not possible without a detailed knowledge of

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8) R. P. Auty and R. H. Cole, *J. Chem. Phys.*, **20**, 1309 (1952).

9) W. Reddish, *Trans. Faraday Soc.*, **46**, 459 (1950).

* In spite of their interpretation, it is difficult for us to find any discontinuing behavior of absorption curves given by them, during the sorption of water.

10) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

11) H. Fröhlich, "Theory of Dielectrics" Oxford Press (1949), p. 53–61, 132.

the micell structure, our results are interpreted qualitatively by Fröhlich's theory. One of the equilibrium positions of the hydroxyl group is more stable than the other. In other words, the arrangement of the hydroxyl group is considered to be well-ordered in the micell of starch and to be somewhat disordered with increasing temperature. The fact that the temperature coefficient of ε_s is positive, means that an external field increases the entropy[12]. This indicates also the possibility that in the absence of the field the hydroxyl group in the micell is well-ordered as may be expected in a crystalline solid.

Abadie et al.[13] found also that $\varepsilon''_{\max}$ of cellulose and starch increases with increasing temperature, and interpreted that these temperature effects were due to the diminution of the action of the environment on the rotation of the hydroxyl groups.

For the α-modification, the relation between the ε' and ε'' was not so satisfactorily represented by the circular arc as for the β-modification and this fact seemed to arise from the relatively large experimental error due to the small volume fraction of the α-modification. Since, however, as can be seen in Fig. 4, the $\varepsilon''_{\max}$ value for the α-modification remains almost constant regardless of temperature, it seems plausible that the arrangement of the hydroxyl group for the α-modification is not so well-ordered as for the β-modification. The present conclusion coincides with the opinion[14] that the α-modification used here is amorphous.

Summary

Dielectric measurements have been made on α- and β-modification of potato starch containing 0.0—17.7% sorbed water in the frequency range from 2 kc. to 3 mc. and temperature range from room temperature to —70°C. The dielectric relaxation process found has been attributed to the hindered rotation of the hydroxyl groups of starch and sorbed water. The heat of activation for this process is about 11 kcal./mole as a mean. The free energy of activation and the mean relaxation time of this process are lowered as the sorbed water is increased. The variation of the dielectric loss curve with the sorbed water has been discussed. Both modifications show similar dielectric behavior qualitatively, except in the case of the temperature dependence of $\varepsilon''_{\max}$ value. The variation of the $\varepsilon''_{\max}$ value with temperature for β-modification suggests that the arrangement of the hydroxyl group would be considerably well-ordered in the micell of starch granule.

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[12] reference 11) p. 9-13.

[13] P. Abadie, R. Charbonnière, A. Gidel, P. Girard and A. Guilbot, *Compt. rend.*, **241**, 1137 (1955).

[14] V. J. Katzbeck and R. W. Kerr, *J. Am. Chem. Soc.*, **72**, 3208 (1950).