*Dielectric Properties of Starch. I. Audio Frequency Region**

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It is well known that there are two modifications of starch, so-called α-modification (gelatinized starch) and β-modification (native starch) which produce different types of X-ray diffraction pattern, the V for the former and the A, B or C for the latter. They also show quite different behavior towards water.

Dielectric measurements have been an effective method for the studies of the sorbed vapors of polar compounds, particularly water, on the various high polymers[1]. However, there have been few dielectric studies of starch, especially for α-modification, except the report by

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1) In connection with the problem of bound water, some attention has been given to dielectric method, for example, see a review by K. Higasi, *Monogr. Res. Inst. Appl. Elec., Hokkaido Univ.*, No. **5**, 9 (1955); "Chemistry of Protein" (Edited by S. Mizushima & S. Akabori), Vol. 4, p. 126 (1956) (Japanese), Kyôritsu Shuppan Co. Ltd., Tokyo.

Shikata and Ueda[2] in 1937 and a rather recent one by P. Abadie et al.[3]. Although we have reported briefly[4] on the same problem, it may be desirable to carry out more detailed studies in wider temperature and frequency ranges and to attempt to find some information on the difference in the configuration between the two modifications.

Experimental

Electrical.—The Schering type bridge[5] used in this study was designed to eliminate errors arising from stray capacitance by use of the Wagner earth[6] (Fig. 1). When the bridge is

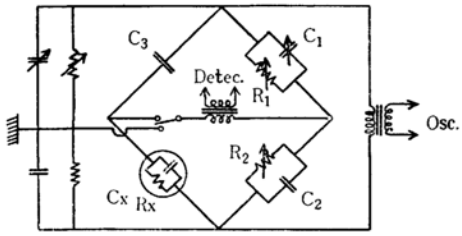

Fig. 1. Schering bridge.

C_x, R_x: equivalent capacitance and resistance of dielectric cell
C_1: maximum 850 $\mu\mu F$, variable air condenser
C_2: 225 $\mu\mu F$, mica condenser
C_3: 350 $\mu\mu F$, air condenser
R_1, R_2: 10-100 kΩ variable resistance

balanced finally, the loss tangent, $\tan\delta$, and the capacitance, C_x, of the dielectric cell are related to the other bridge elements through the equations

$$\tan\delta=\frac{1}{\omega C_x R_x}=\left(\frac{C_1R_1}{C_2R_2}-1\right)\Big/\left(\frac{1}{\omega C_2R_2}+\omega C_1R_1\right) \quad (1)$$

$$C_x=\left(\frac{C_3R_1}{R_2}\right)\left(\frac{1}{1+\omega C_1R_1\tan\delta}\right) \quad (2)$$

where ω is 2π times the frequency.

Since we made no attempt to prevent the inductive effects, the upper limit of frequency was about 30 kilocycles per second. The lower limit of frequency was influenced by the character of the detector, and 500 cycles per second was the lower limit in our case. In this frequency range experimental errors of measurements were within $\pm1.0\%$ and $\pm3.5\%$, for capacitance and loss tangent respectively.

Dielectric constant, ε', and loss factor, ε'', are calculated from the value of C_x and $\tan\delta$, by the following equations.

$$\varepsilon'=C_x/C_0 \quad (3)$$

$$\varepsilon''=\varepsilon'\tan\delta \quad (4)$$

where C_0 is the capacitance of the empty cell.

Dielectric Cell.—The cell used is shown in Fig. 2. It consisted of two concentric glass

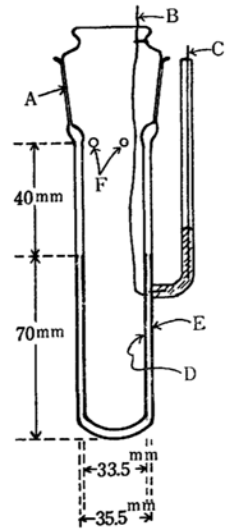

Fig. 2. Dielectric cell.

A is a taper ground-glass joint, D and E are copper electrodes connected to the lead wires B and C respectively through platinum seals, and F is a small orifice made on inner cylinder from which air is removed.

cylinders connected at a taper ground-glass joint. Copper electrodes were made by plating on the silver plates which were deposited on the ground glass walls.

Materials.—Since, as we already reported[4], no remarkable difference has been found between the dielectric properties of various kinds of starch (potato, waxy rice, lily bulb and potato amylose); both modifications of potato starch were only investigated in this study. The β-modification was pharmacopoeial grade. The α-modification was prepared by Onishi Syokuhin Co. Ltd., according to the following method. Gelatinized sol of pharmacopoeial grade starch was dried by heated rolls and ground to fine powder. According to Katzbeck et al.[7], thus prepared α-modification seems amorphous. The liquid paraffin used was the fraction distilled at temperatures between 170°—250°C under 5 mmHg pressure, and was loss free within the experimental error.

Procedures.—Starch was dried in an oven at 100°—105°C until constant weight was reached. The starch conditioned in this way was regarded as dry starch, although a small quantity of water could still remain. The water content of the sample was determined by weighing the increasing weight after the starch was exposed to the

2) M. Shikata and S. Ueda. *J. Electrochem. Assoc. Japan*, **5**, 438 (1937).
3) P. Abadie, R. Charbonnière, A. Gidel, P. Girard and A. Guilbot, *J. Chim. Phys.*, **50**, C46 (1953).
4) N. Koizumi, S. Ono and T. Kuge, *Bull. Inst. Chem. Research, Kyoto Univ.*, **22**, 80 (1950).
5) R. M. Fuoss, *J. Am. Chem. Soc.*, **59**, 1703 (1937).
6) D. Owen, "Alternating Current Measurements", Methuen & Co. Ltd., London (1950) p. 57.
7) W. J. Katzbeck and R. W. Kerr, *J. Am. Chem. Soc.*, **72**, 3208 (1950).

atmospheric moisture. The starch dispersed in liquid paraffin was poured in the sample space of the cell. The cell was then evacuated to remove the air which is contained in the sample. The dielectric measurements were carried out, after the cell had been kept for two days to sedimentate the starch spontaneously to the lower part of the cell where electrodes were placed. The method described above was convenient to keep the water content constant during the measurement, but has the disadvantage that we can not make the volume fraction of the starch between the electrodes a given desired value. The volume fraction of each sample was estimated from the sedimentation volume of the starch of a known weight by using a graduated sedimentation tube whose diameter was about 1 cm.

An insulating oil bath fitted with a small electric heater was used to control the temperature during the measurements at temperatures higher than room temperature. At lower temperatures a Dewar flask filled with ethanol was employed as a bath which was cooled by dry ice. The temperature inside the cell was adjusted to the bath temperature within one degree, and all measurements were made as a function of frequency at fixed temperatures.

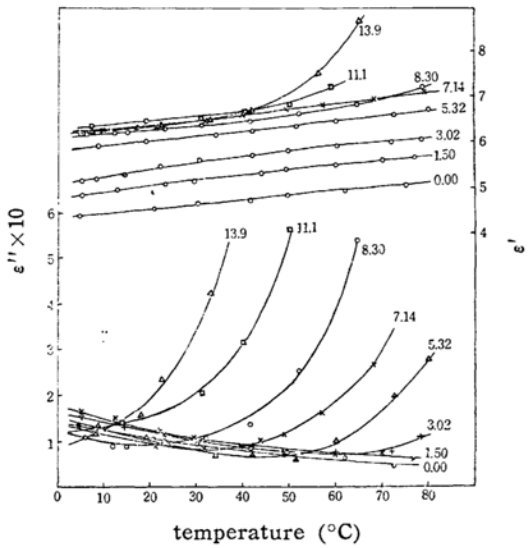

Fig. 3. Variations of ε' and ε'' with temperature at 4 kc. for β-modifications of potato starch containing sorbed water at the inscribed amounts (g./100 g. dry starch).

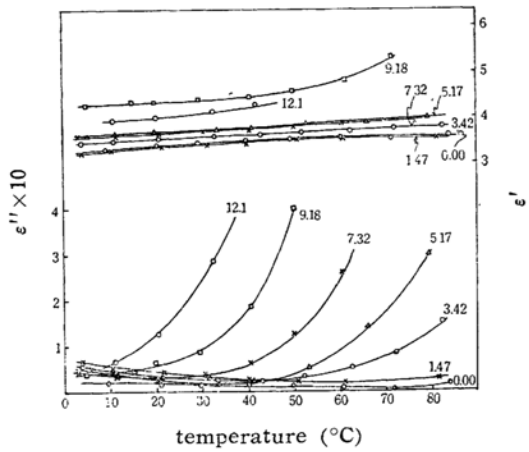

Fig. 4. Variations of ε' and ε'' with temperature at 4 kc. for α-modifications of potato starch containing sorbed water at the inscribed amounts (g./100 g. dry starch).

Results and Discussion

Some typical results of the measurements are shown in Figs. 3—7. Figs. 3 and

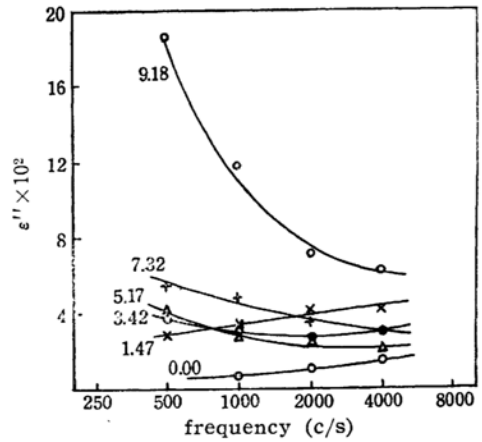

Fig. 5. Frequency dependence of ε'' of α-modifications containing sorbed water at the inscribed amounts (g./100 g. dry starch) at room temperature.

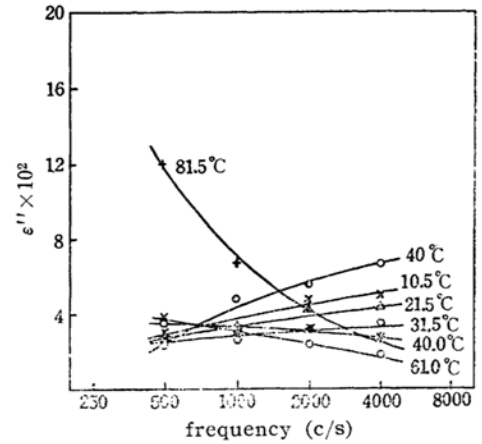

Fig. 6. Frequency dependence of ε'' of α-modification containing 1.47% water (g./100 g. dry starch) at various temperatures.

4 show the results obtained at 4 kc. for β- and α-modification of potato starch respectively which contained various amounts of water. The temperature coefficients of ε' were always positive. The ε'' value of each sample decreased with increasing temperature until a certain temperature was reached, and thereafter began to increase sharply. The more water the sample contained, the lower the temperature became. ε' became larger as the water content was increased. Frequency dependence of ε'' of α-modification is shown in Figs. 5 and 6. The sharp increase of ε'' found in the lower frequency region may be ascribed to the mechanism which causes a similar increase in the higher temperature region as shown in Figs. 3 and 4. We call this loss process "the low frequency loss process of starch". This loss process is affected markedly by the sorption of water. Similar phenomena have been observed in the case of cellulose[8] and wood[9].

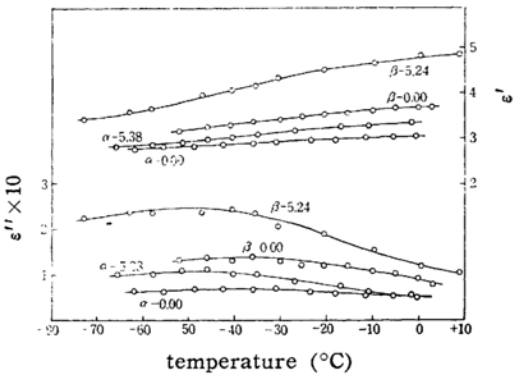

Fig. 7. Variations of ε' and ε'' of potato starch with temperature at 4 kc.

β-0.00 and β-5.24 express β-modifications containing 0.00 and 5.24% water (g./100 g. dry starch) respectively; α-0.00 and α-5.38 express α-modifications containing 0.00 and 5.38% water (g./100g. dry starch) respectively.

Fig. 7 shows the results obtained in the low temperature range, i.e., from room temperature to −70°C at 4 kc. It can be seen from Fig. 7 that each curve of ε'' appears to have a maximum at −40° to −50°C, although the maximum region is broad. In such a temperature region, ε' shows somewhat steep changes with temperature. We call this dielectric dispersion "the high frequency loss process of starch" on which we shall discuss in detail, using results in radio frequency region, in the following paper. This process may be attributed to dipole orientation of hydroxyl group.

On examination of the curves shown in Figs. 3, 4 and 7, it may be concluded that both modifications of starch have qualitatively the similar dielectric properties. Different numerical values of ε' and ε'' between both modifications appear to be caused mostly by the difference between their volume fractions.

It may be difficult to see to what extent the loss due to direct current conduction, interfacial-polarization (Maxwell-Wagner type) or usual dipole orientation (Debye type) contributes to the low frequency loss process. Among these effects, however, direct current conduction, due to inorganic ions adsorbed on the native starch granules, may probably be able to give most of the loss of the low frequency loss process. In order to test this possibility, log ε'' was plotted against log f(f is the frequency.). These plots gave almost straight lines with a slope −0.65 to −0.75 in the region where the low frequency loss process was distinctly observed***. This fact suggests that direct current conduction effect may be associated with an additional alternative current behavior, since the theoretical slope would be −1, if direct current conduction were only the cause of the low frequency loss process. It seems most likely that the Maxwell-Wagner type loss is superposed on the direct current loss in a similar manner to the case of terylene described by Reddish[10]. More detailed discussion on the low frequency loss process is difficult, because direct current and lower frequency measurements are not available in our study. Shikata and Ueda[2] found a maximum loss tangent of starch at frequencies less than 1 kc. and explained it by means of dipole orientation of water sorbed on starch granule. However, according to our interpretations, their results should correspond to the low frequency loss process, so that the larger orientational unit (e.g. glucose, glucose chain etc.) than the one that they proposed should be considered as the cause of the dielectric loss even if Debye type loss is postulated.

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

9) L. Pungs, *Electrotech. Z.*, **A75**, 433 (1954).

*** A. Similar behavior concerning the frequency dependence of ε'' at low frequencies has been found for many other dispersed systems; R. Gotoh, T. Hanai and N. Koizumi (to be published).

10) W. Reddish, *Trans. Farady Soc.*, **46**, 459 (1950).

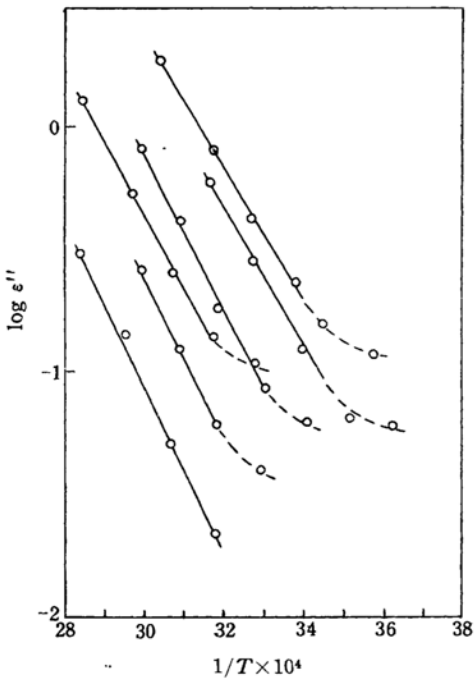

Fig. 8. Plot of log ε'' against $1/T$ at 4 kc. $\alpha-5.17$, $\alpha-7.32$, $\beta-8.30$, $\alpha-9.18$, $\alpha-12.1$ and $\beta-13.9$ in order from left to right.

In Fig. 8 log ε'' was plotted against reciprocal absolute temperature and linear relations were found when the influence of the high frequency loss process was allowed for. The activation energies of conduction in the low frequency loss process were calculated from these plots to be 15–12 kcal./mole, being smaller as the water content is increased. Although physical meanings of these energies are not obvious, it is mentioned that the values of the similar magnitude are obtained for both α- and β-modification.

It is favorable for the investigation of the properties of sorbed water to calculate its polarization. Since dielectric constants and loss factors hitherto described are those of starch-liquid paraffin systems having different volume fractions (Table I), the dielectric constant of starch itself (including sorbed water), ε_a was evaluated from the observed values ε', by using Kamiyoshi's formula[11]. The calculated value of ε_a was inserted into the following Kirkwood's formula[12] in order to obtain the specific polarization, P_a,

$$P_a=\frac{(\varepsilon_a-1)(2\varepsilon_a+1)}{9\varepsilon_a}\frac{1}{d} \qquad (5)$$

11) K. Kamiyoshi, *Sci. Rep. Res. Inst. Tohoku Univ.* **A2**, 180 (1950).
12) J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939); *Trans. Faraday Soc.*, **42A**, 7 (1946).

where d is the density of starch measured by means of picnometer using toluene as an immersion medium. These values are shown in Table I. Assuming that the additivity of the polarization holds

$$P_a=P_sW_s+\sum P_iW_i \qquad (6)$$

$$W_s+\sum W_i=1 \qquad (7)$$

where P_s and W_s are the specific polarization and the weight fraction of starch alone respectively, P_i and W_i are the specific polarization and the weight fraction of the i th component of the sorbed water. If P and P_i are independent of each other, then from Eqs. (6) and (7)

$$\partial P_a/\partial W_i=P_i-P \qquad (8)$$

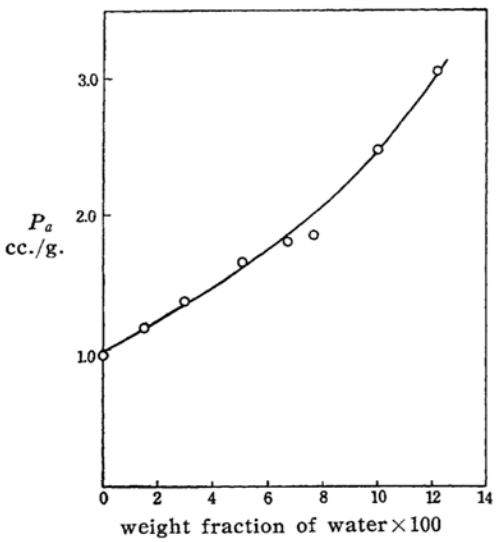

Fig. 9. Relation between the specific polarization and water content of potato starch at 20°C, 4 kc.

TABLE I

WATER CONTENT, DIELECTRIC CONSTANT AND POLARIZATION FOR β-MODIFICATION OF POTATO STARCH CONTAINING SORBED WATER AT SEVERAL DIFFERENT AMOUNTS

frequency: 4 kc., temperature: 20°C

Water content g./100g. dry starch	Volume fraction of starch	d g./cc.	ε'	ε_a	P_a cc./g.	P_i cc./g.
0.00	0.56	1.540	4.53	7.38	0.98	12.1
1.50	0.56	1.540	5.01	8.68	1.17	
3.02	0.55	1.535	5.40	10.0	1.36	
5.32	0.55	1.530	6.00	11.9	1.65	14.9
7.14	0.55	1.524	6.34	13.0	1.82	
8.30	0.54	1.520	6.26	13.1	1.84	
11.1	0.47	1.510	6.42	17.4	2.48	23.2
13.9	0.42	1.490	6.33	21.1	3.06	

Fig. 9 shows the variation of P_i with water content at 20°C and 4 kc. We can calculate P_i (given in Table I) from the slope at each point on the best smooth curve drawn through the experimental points, when the observed value for the dry sample is used as P_s. P_i increases gradually from 12.1 cc./g. for the dry sample to over 23.0 cc./g. for the higher water content so that we can not distinguish the sorbed water in various sorption states, according to the sorbed amount. Windle and Shaw[13] obtained a curve for wool similar to that in the present results and estimated the molar polarizations of the localized and the mobile water separately, using Cassie's results concerning water absorption. On the other hand, in the case of silica gel, Kurosaki[14] found that three different states of sorbed water were separately observed by the bending points of dielectric constant vs. water content curve. These facts seem to show the different ways of the sorptions corresponding to absorption and adsorption respectively. For comparison, polarization of water in various states is given in Table II. At first glance it may seem

TABLE II

SPECIFIC POLARIZATION OF WATER IN VARIOUS STATES

Adsorbent	Frequency and temperature	Specific polarization cc./g. 1	8–15	17.7	22–23
water	static			liquid water	
starch	4 kc. 20°C		0–5% sorbed water		10% sorbed water
wool[13]*	3×10^8 mc. 25°C	bound water	mobile water		
silica gel[14]	5 kc. 25°C	0–1.5% water of 1st sorption	2–8% water of 2nd sorption		10% water of 3rd sorption

* Recalculated from molar polarization. The values at audio frequency should be larger than the above ones.

that water would not be so strongly absorbed on starch as on wool or silica gel, because there is no water having P_i of about unity in our case****. According to the absorption theory[15], however, it seems reasonable that water sorption occurs at various sites distributed throughout starch, and water molecules restricted in different strengths exist simultaneously in any sorption stage. Therefore, P_i should be regarded as the mean polarization of the sorbed water. From the continuous change of P_i, it may be merely concluded that the fraction of the less firmly bound water gradually increases as sorption proceeds. It is unable to estimate the polarizations of localized (bound) and mobile (free) water separately without the knowledge of their fractional numbers. The fact found by Sato[16] that the heat of the water sorption by starch decreases with increasing sorption without discontinuous points, seems to be in good agreement with our observation.

The sorbed water of about 10% or more has a larger polarization value, i.e., 23 cc./g. or more, than that of liquid water. There are two ways in which these large polarizations may be explained. One is to consider a much more highly developed hydrogen bond than that of liquid water, and the other is to consider that P_s is not constant as was assumed in the derivation of Eq. (8), but must increase with increasing water content. The latter may be more plausible for starch, since water molecules seem to penetrate into the starch granule throughout and to loosen the secondary force which is associated with micell formation[15]. In other words, the polar group of starch becomes more polarizable, while the penetrating water loosens the micell structure.

Since the reproducibility of the volume fraction measurement was insufficient in the case of α-modification, calculations of P_i were not performed.

Summary

The results of dielectric measurements for α- and β-modification of potato starch containing 0.0–13.9% sorbed water at audio frequency region are described. At different temperature regions, two different dielectric loss processes are found which we call low frequency loss process and high frequency loss process. Discussions on the low frequency loss process are made. Qualitatively, both modifications of starch have the similar dielectric properties. From the analysis of the

13) J. J. Windle and T. M. Shaw, *J. Chem. Phys.*, **22**, 1752 (1954).
14) S. Kurosaki, *J. Phys. Chem.*, **58**, 320 (1954).
**** Water which still remains after the heating procedure at 105°C is not taken into consideration.
15) 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).
16) H. Sato, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 790 (1951).

polarization of the sorbed water, it may be concluded that sorbed waters change their properties gradually as sorption is increased, while they also loosen the micell structure of starch.

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