The Changes in Dielectric Properties of Water during Adsorption by Solids

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(Recieved 18 June 1964)

1. Introduction

Kurosaki et al.[1] found that when glass cloth was exposed to water vapour, its tan δ rapidly increased to a maximum and then gradually decreased to a constant value, and that the surface dc conductivity of glass and some other substances showed similar changes on exposure to water vapour. These investigators attributed the phenomena to phase changes of the adsorbed water from the amorphous to the crystalline state. Similar time effects with evaporated films were reported by Weaver[2], who considered that the capacitance and tan δ reached their peak values when adsorption was complete, and that some gradual rearrangement of the adsorbed water molecules then took place which reduced their effect on the overall dielectric properties. The present authors found that a time effect, somewhat different from those of Kurosaki et al. and Weaver, was produced when moisture was transferred to a specimen placed in dry air, instead of a vacuum as in the cases cited above. Outlined in the present article are the comparison of the results obtained when a specimen is placed in a vacuum and dry air respectively, and some explanation of the changes occurring in dielectric properties of water during adsorption by solids. The measurements were made on soda lime glass, mica, porous calcined diatomaceous earth, and filter paper, but as the results are generally alike in all of them, those obtained with soda lime glass are described in detail, and the others only briefly.

2. Experimental Procedure

It was devised to make the chamber (A) containing the specimen as small as possible to eliminate useless space. By a leak cock system the chamber could be connected with :

(B) a vacuum pump working at 10^{-2}mmHg,
(C) a large chamber containing dry air over concentrated sulfuric acid, or
(D) a large chamber containing air of specified humidity,
or cut off from all of them.

Before taking measurements, the chamber (A) was connected with (B) for an hour, or with (C) for 24 hours. We call these as case 1 and case 2 respectively in the following. The capacitance measurements were carried out at frequencncies as low

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as 3 c/s by the apparatus described previously[3][4], because the time effect during adsorption of water was especially conspicuous at very low frequencies. The surface dc conductivity was measured with a $\mu\mu$ ammeter of the Toa Dempa Co.

The electrodes for the dielectric measurements were set as follows. For glass or mica two aluminum foils seperated by a slit were attached on the surface with water and dried, for calcined diatomaceous earth, a coating of silver paste was given to each surface of the plate and fired, and for filter paper, two patches of air-drying silver paste were painted on one surface with a slit between them.

3. Results and Discussion

In the following the results are divided in two cases :

(Case 1) Moisture is transferred to a specimen placed in a vacuum.

(Case 2) Moisture is transferred to a specimen placed in dry air.

Soda lime glass

The slit between the electrodes was 0.37mm wide and 80mm long.

(Case 1)

The curves (a), (b) and (c) given in Fig. 1 show the changes of capacitance of the glass plate observed after admission of humid air.* The capacitance increases rapidly to a peak and then gradually decreases to a certain value and begins to increase again very slowly. These results resemble the experimental results obtained by Weaver with thin evaporated films. When the leak cock was closed at the time of peak, the capacitance was found to remain almost unchanged, but when the cock was opened again the capacitance began to change as curve (d) in Fig. 1. Therefore the adsorption should not be regarded as complete at the time of maximum capacitance, but to proceed still further after that. When the leak cock was closed at any time while the capacitance was ascending to the peak or descending from it the capacitance stopped changing and remained as it was. When the glass plate with adsosbed water was dried very slowly by connecting (A) and (C) through a pinhole of the leak cock, the capacitance changed as shown in Fig. 2. The peak in this case perhaps corresponds to the peak in the adsorption, and seems to be due to the same cause. Fig. 3 shows the time dependence of surface dc conductivity of a sample of glass. Curves (a) and (b) correspond respectively to the cases where the diameter of the pinhole of the leak cock is 0.35mm and 0.10mm. Such time effect in the surface dc conductivity has some resemblance to the results obtained by Kurosaki et al. with glasses of different kinds. When the leak cock was closed at any time before the conductivity reached the peak, it stopped ascending and remained almost un

* The results described hereafter were obtained with air of 93% relative humidity except where indicated otherwise.

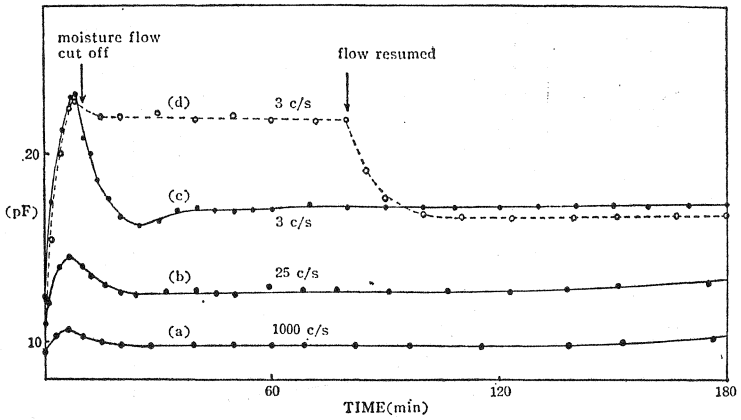

Fig. 1 Capacitance changes during moisture adsorption measured at the frequencies indicated. (soda lime glass)

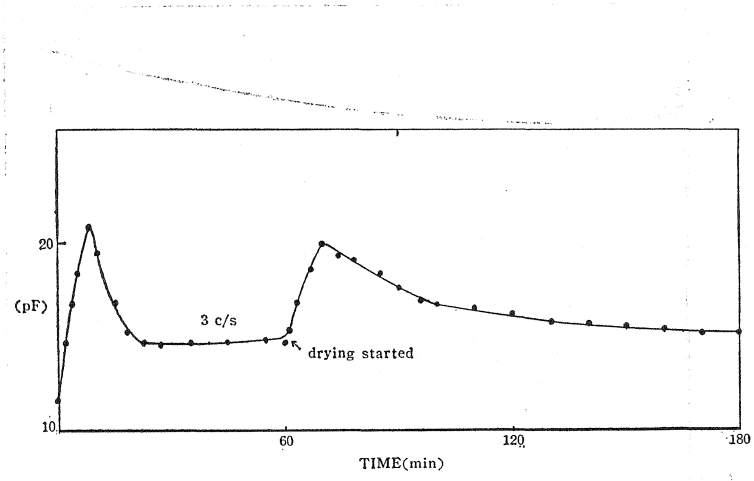

Fig. 2 Capactance changes when a glass plate with adsorbed water was slowly dried. (soda lime glass)

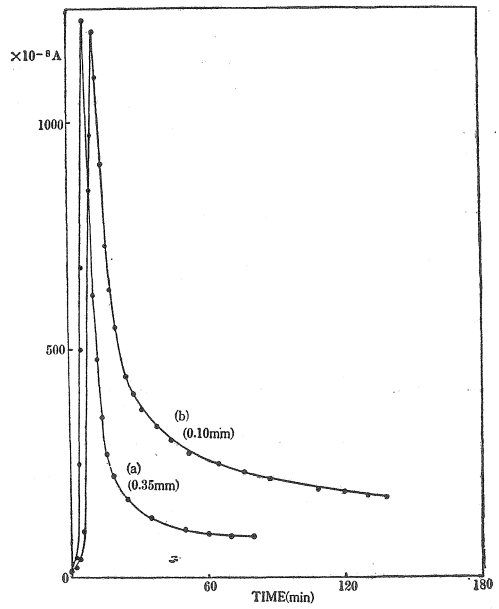

Fig. 3 Surface conductivity changes during moisture adsorption. (soda lime glass)

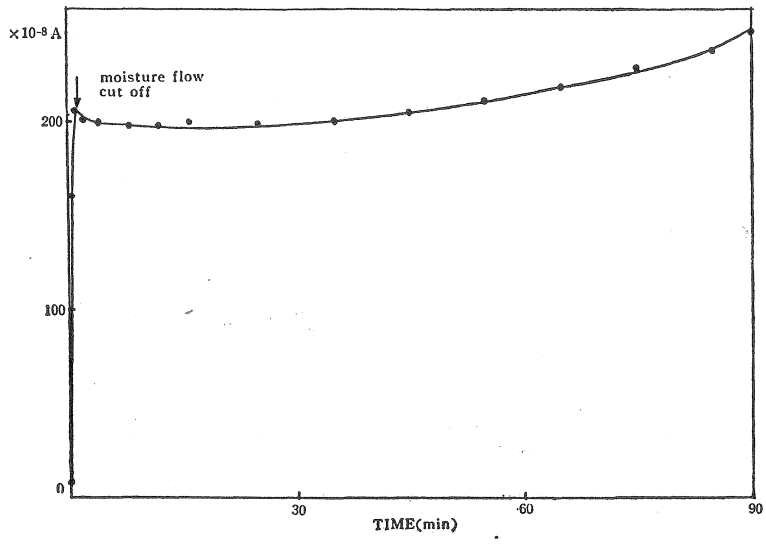

Fig. 4 Surface conductivity changes when moisture flow was cut off before it reached the peak. (soda lime glass)

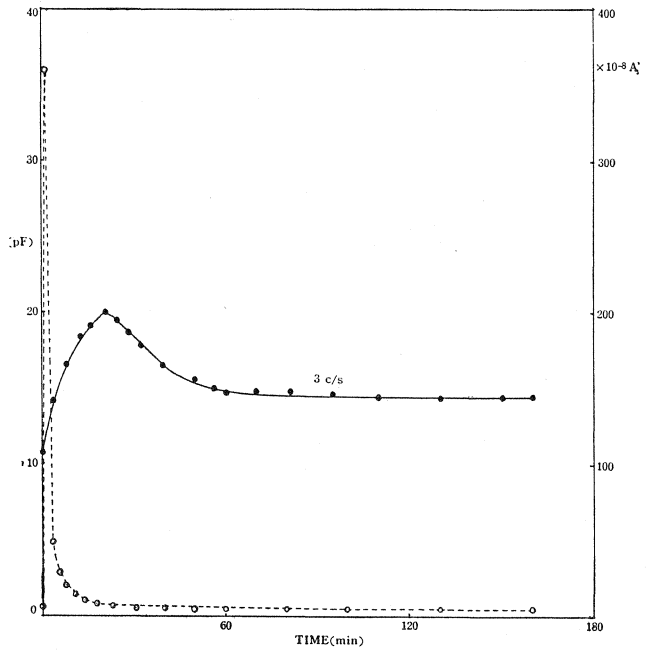

Fig. 5 The result of a simultaneous measurement of the capacitance and conductivity. (soda lime glass) Solid curve : Capacitance, Broken curve : Conductivity.

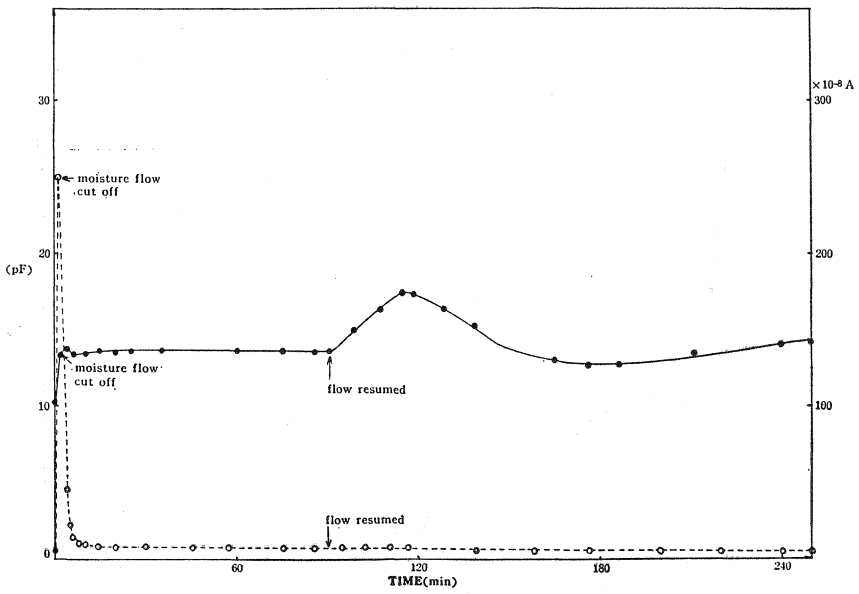

Fig. 6 The result of a simultaneous measurement of the capacitance and conductivity when moisture flow was cut off at the time of peak of the conductivity. (soda lime glass)

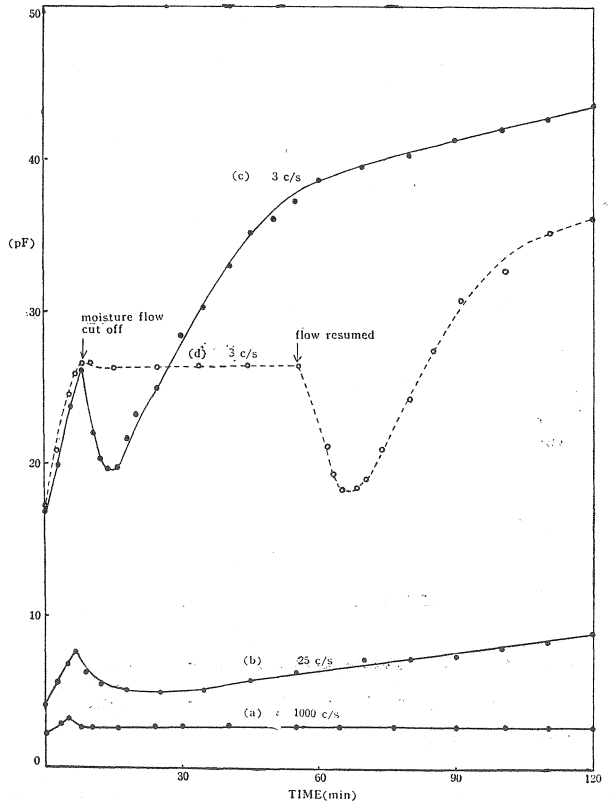

Fig. 7 Capacitance changes during moisture adsorption measured at the frequencies indicated. (soda lime glass)

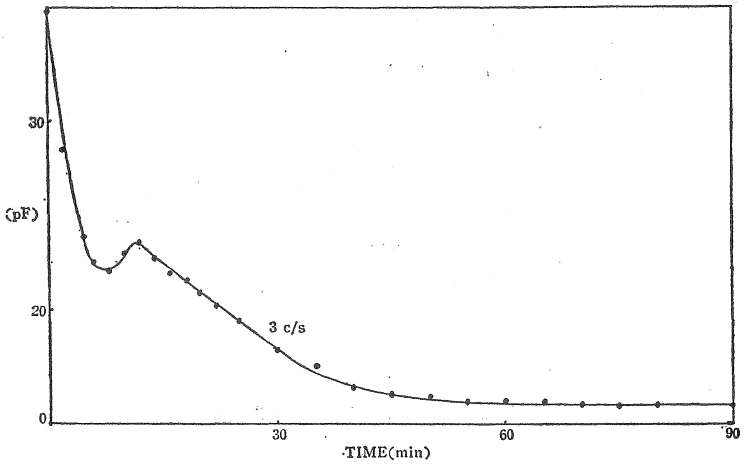

Fig. 8 Capacitance changes when a glass plate with adsorbed water was slowly dried. (soda lime glass)

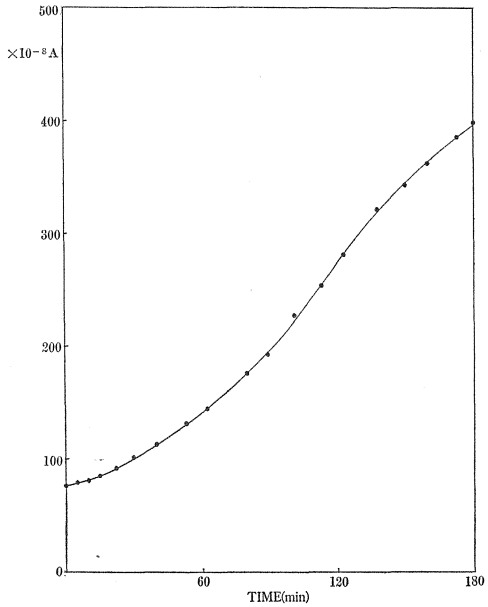

Fig. 9 Surface conductivity changes during moisture adsorption. (soda lime glass)

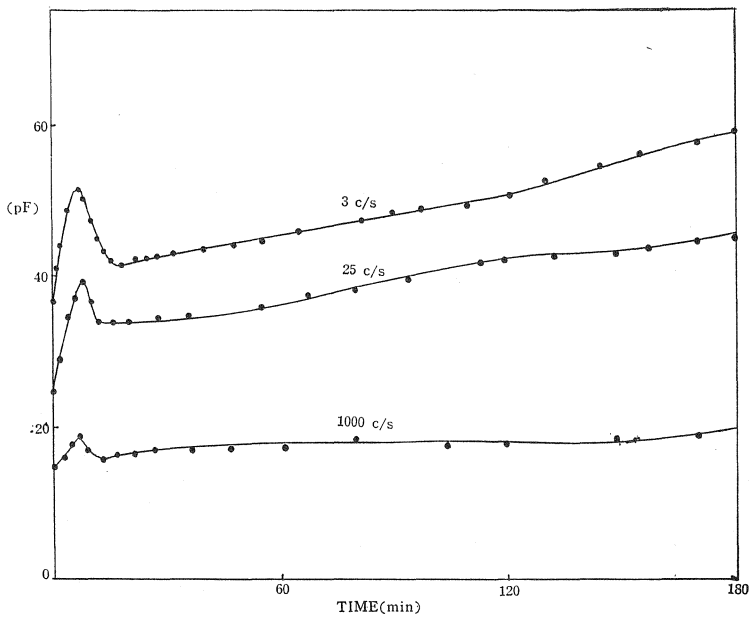

Fig. 10 Capacitance changes during moisture adsorption measured at the frequencies indicated. (mica)

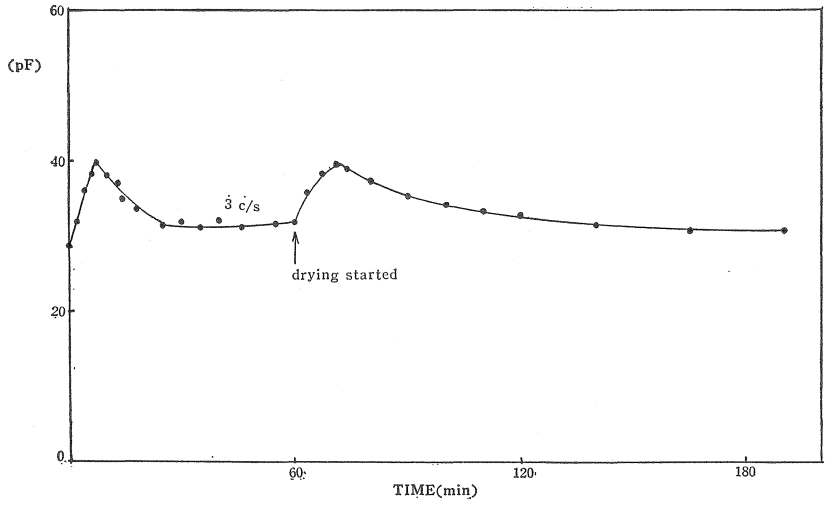

Fig. 11 Capacitance changes when a mica plate with adsorbed water was slowly dried. (mica)

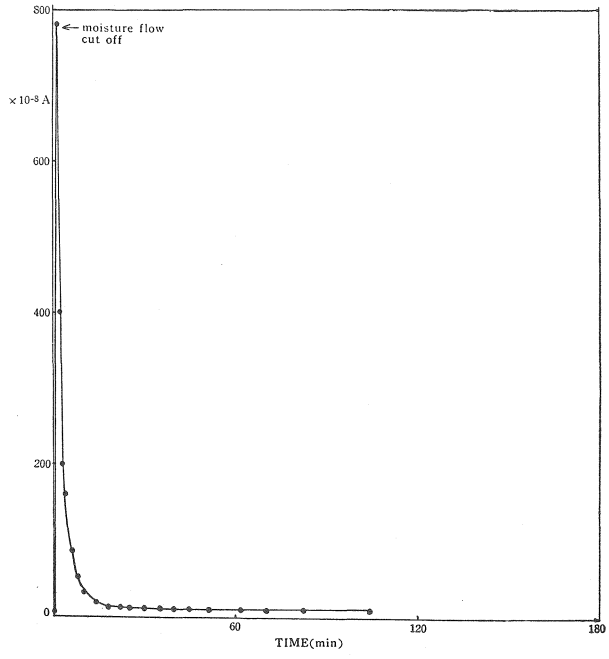

Fig. 12 Surface conductvity changes when moisture flow was cut off at the time of the peak. (mica)

changed as shown in Fig. 4, but when the cock was closed at the time of the peak the conductivity decreased abruptly as in the case it was kept open. These results were thought to show that different mechanisms are involved in the changes of capacitance and conductivity of the water during adsorption. This supposition was confirmed by carrying out simultaneous measurement of the capacitance and conductivity. The result is shown in Fig. 5 and Fig. 6, from which we see that the conductivity reaches the peak more quickly than the capacitance, and decreases even if the leak cock is closed at that time.

(Case 2)

The curves (a), (b) and (c) given in Fig. 7 show the changes of capacitance at 93% relative humidity for a glass plate. The capacitances increase rapidly to maximum peaks and then gradually decrease to certain values and begin to increase more rapidly than in case 1. The curve (d) shows the change of capacitance observed when the leak cock was closed at the time of the peak and opened again after about one hour. When a glass plate with ample adsorbed water was dried very slowly, the capacitance changed as shown in Fig. 8. The peak in this case perhaps corresponds to the peak in the adsorption, and seems to be due to the same cause. Fig. 9 shows the time dependence of surface dc conductivity at 93% relative humidity. In this case the conductivity increases monotonously with time, and the curve has no peak.

Comparison of Case 1 and Case 2

The capacitance measured at 3 c/s in case 2 showed conspicuous increase after the minimum. This increase must be due to electrode polarization, which is especially marked at low frequencies and increase with the amount of adsorbed water[5]. In case 1 the adsorption seems nearly to stop after the minimum. It must be due to the better degassing of the glass plate than in case 2. According Trouton[6] as quoted by Kurosaki et al. perfectly dried glass adsorbed water vapour with greater difficulty than imperfectly dried glass, owing to the lack of water nuclei or active sites on its surface. The peak of capacitance appears at an early stage of adsorption in both cases. We presume it to be mainly due to the cooperative orientational polarization of water molecules, which is more notable in a thin layer of water rather than in a thick amorphous layer. The initial peak of the conductivity in case 1 must be due to some mechanism of water film which is far thinner than that for which the peak of capacitance occurs. And the absence of an initial peak in the conductivity in case 2 may be due to the thickness of the water layer exceeding the critical thickness limiting the occurence of the peak at the starting moment of adsorption.

To explain the various phenomena mentioned above we assume the change of the structure of water film during adsorption as follows. In the initial stage of adsorption, mutual hydrogen bonding of adsorbed molecules is still incomplete and there are many gaps in the chains of hydrogen bondings. This situation is favourable for surface dc conductivity by the proton transfer along the chains of hydrogen bondings. In the next stage the hydrogen bondings of water molecules are accomplished which is favourable for electric polarization due to the cooperative displacements of protons, but not for electric conductivity due to proton transfer. After that, as the water film increases in thickness and changes to a nearly amorphous state the electric polarization due to the cooperative displacement of protons tends rather to decrease. But the effect of electrode polarization increases with the thickness of the water film.

Mica

The slit between the electrodes was 0.5mm wide and 80mm long.

(Case 1)

The effect of moisture on mica is shown in Fig. 10 which gives changes in capacitance with time elapsed after admission of moisture. The increase of capacitance after the time of minimum point is more rapid than with glass, showing the difficulty of drying mica completely. The capacitance change which occurs when a mica plate with adsorbed water was dried very slowly is shown in Fig. 11. Closing of the cock at the time of the peak of dc condctivity made it decrease abruptly as shown in Fig. 12.

(Case 2)

The curves shown in Fig. 13 were obtained at 82% relative humidity. When a mica plate with sufficent adsorbed water was dried very slowly, the capacitance changed as the curve in Fig. 14 showing a conspicuous peak.

Calcined diatomaceous earth

The specimen used for our measurements was a plate (1.5mm × 15mm × 8mm). In this case water is adsorbed on the internal surfaces of the porous material.

(Case 1)

The curves in Fig. 15 give the change in capacitance as a function of time after admission of moisture into the evacuated vessel containing the specimen. The result of a simultaneous measurement of the capacitance and dc coductivity is shown in Fig. 16. The conductivity reaches the peak more quickly than the capacitance as in the case for glass.

(Case 2)

Fig. 17 and Fig. 18 show respectively the time dependence of capacitance when

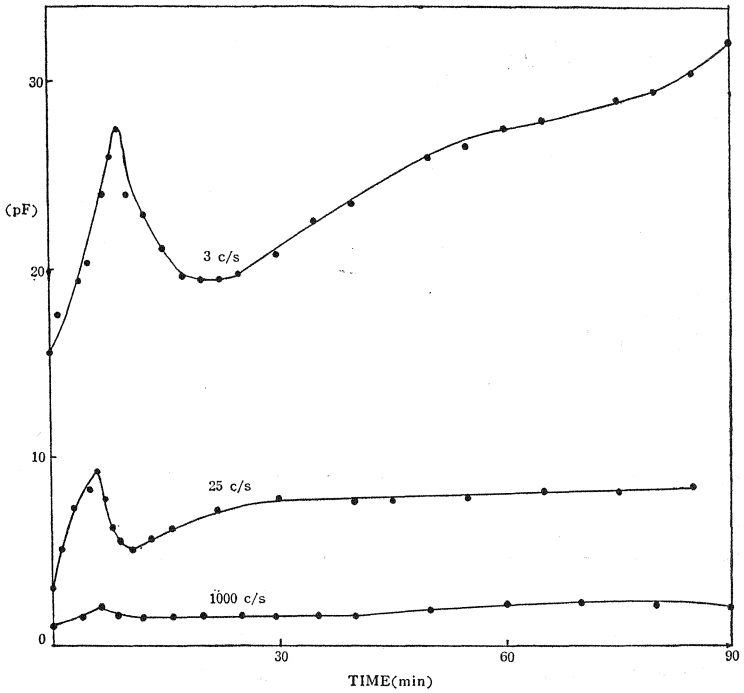

Fig. 13 Capacitance changes during moisture (82% relative humidity) adsorption at the frequencies indicated. (mica)

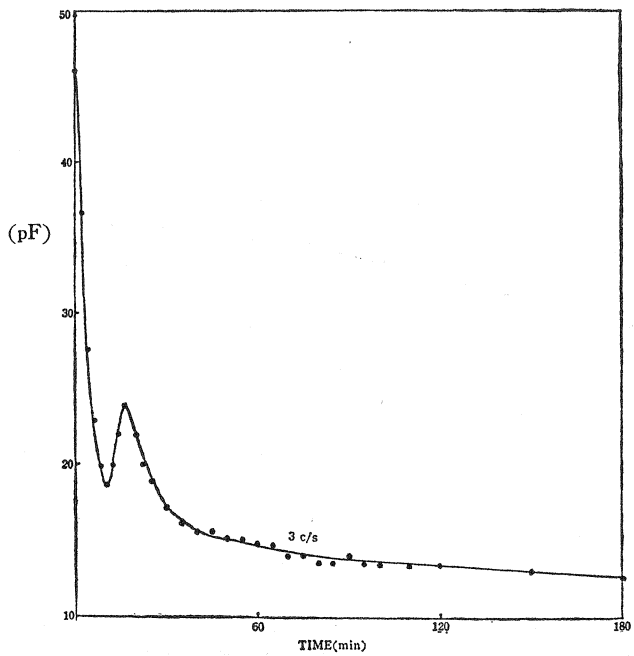

Fig. 14 Capacitance changes when a mica plate with adsorbed water was slowly dried. (mica)

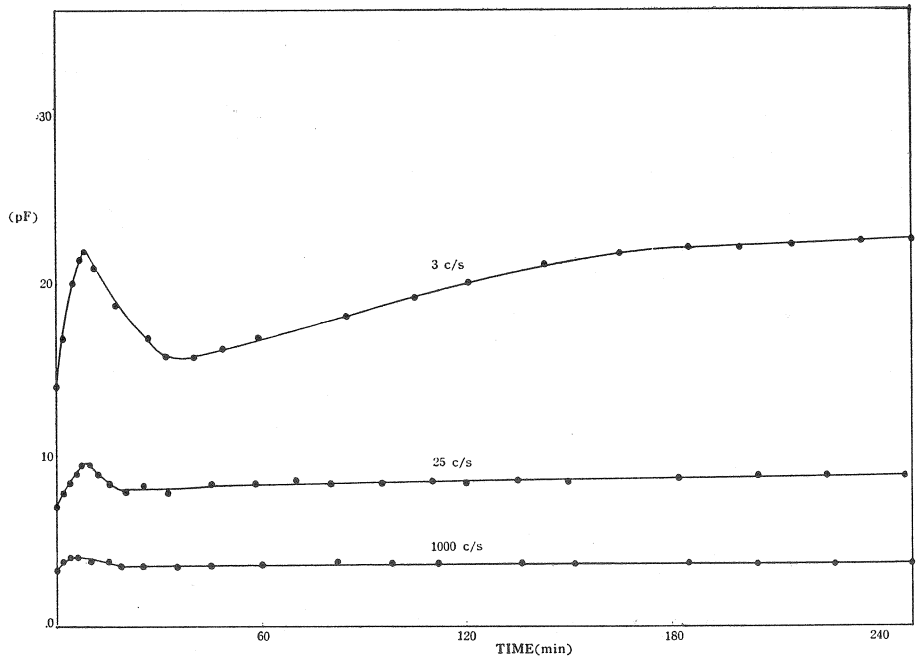

Fig. 15 Capacitance changes during miosture adsorption at the frequencies indicated. (calcined diatomaceous earth)

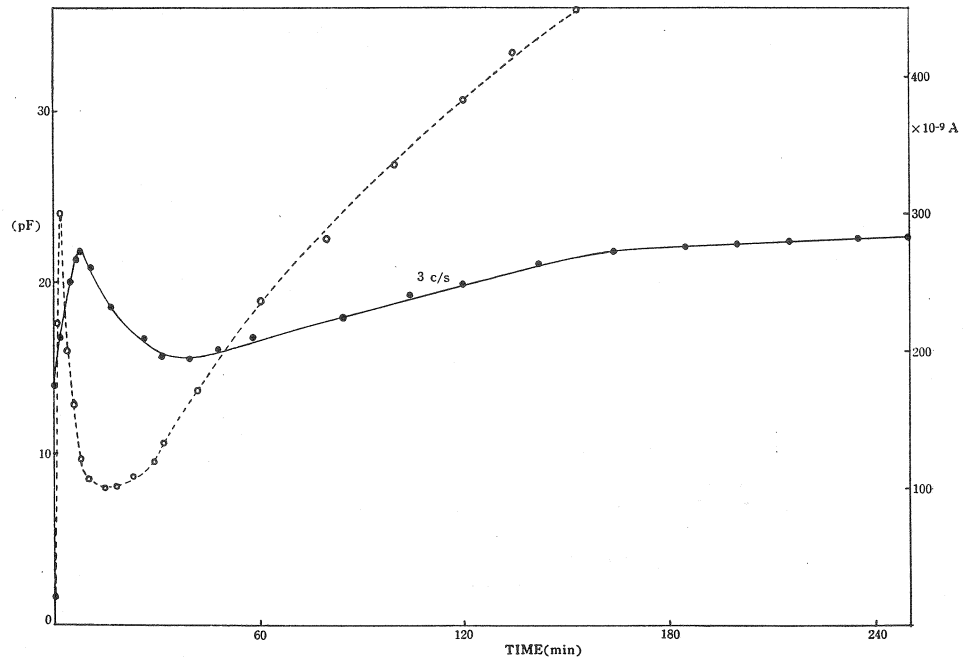

Fig. 16 The result of a simultaneous measurement of the capacitance and conductivity. (calcined diatomaceous earth)

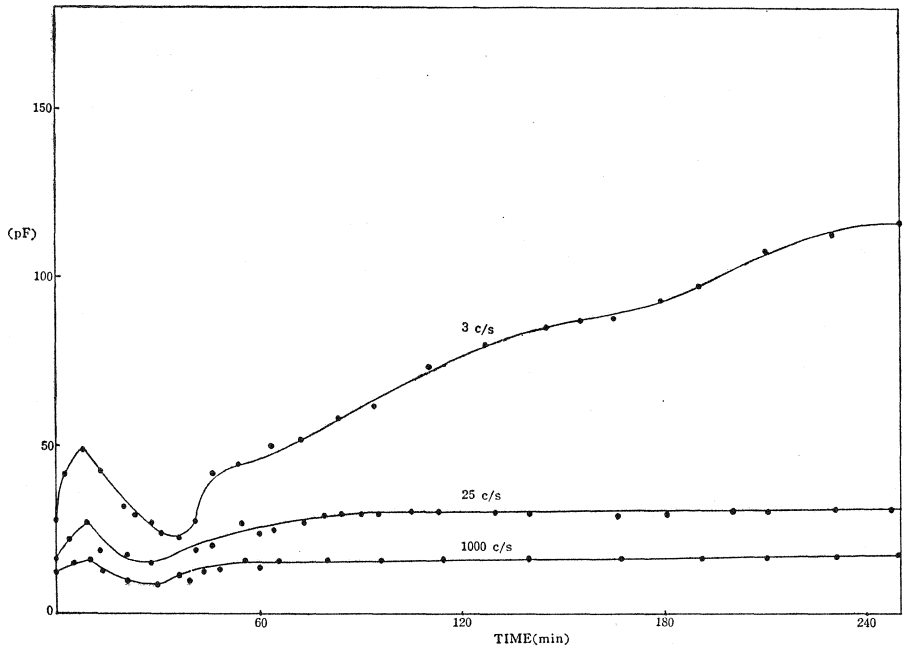

Fig. 17 Capacitance changes during moisture adsorption at the frequencies indicated. (pinhole of the leak cock is 1.5mm in diameter). (cacind diatomaceous earth)

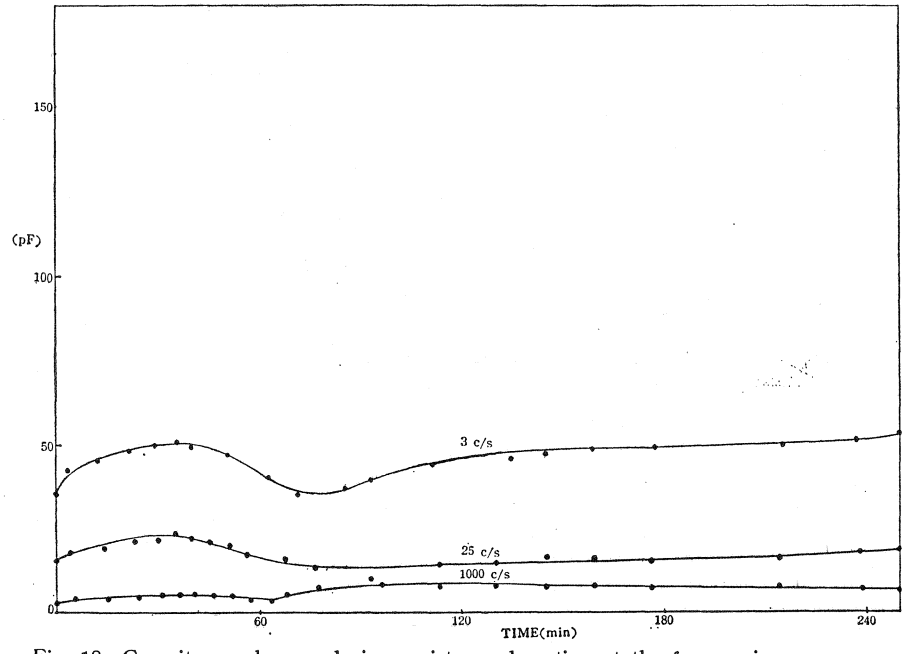

Fig. 18 Capacitance changes during moisture adsorption at the frequencies indicated (pinhole of the leak cock is 0.3mm in diameter). (calcined diatomaceous earth)

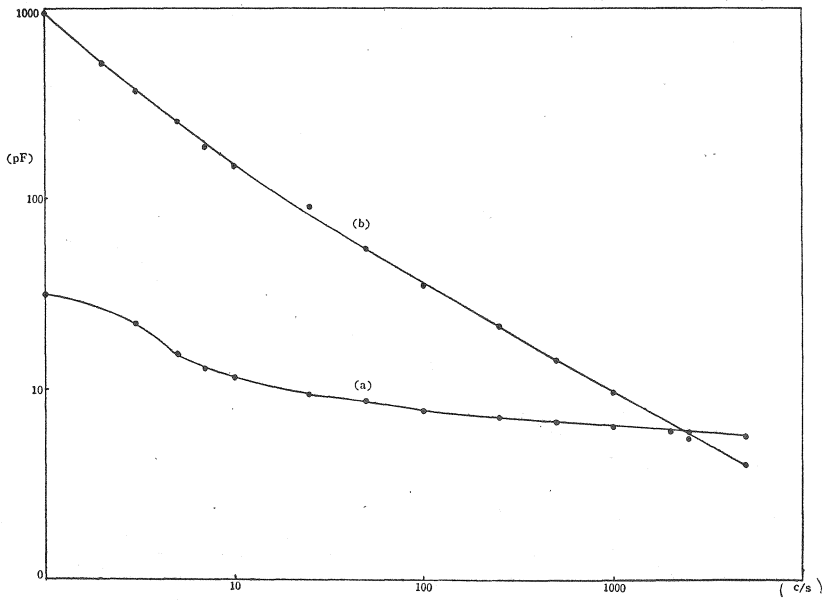

Fig. 19 Frequency dependences of the capacitance.
(calcined diatomaceous earth)

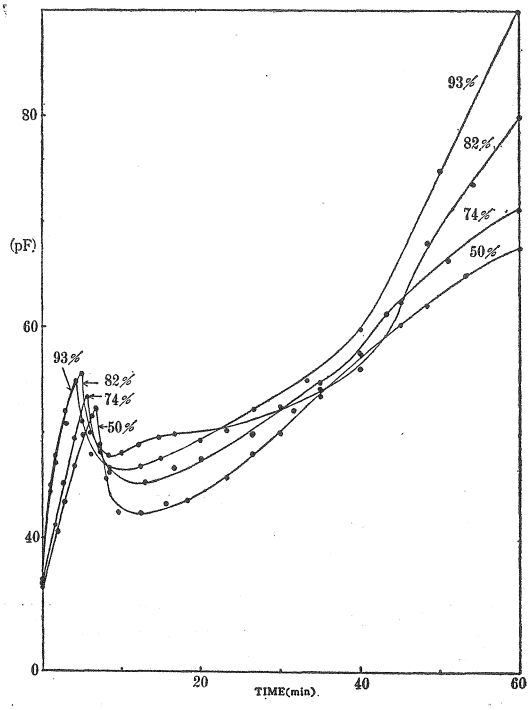

Fig. 20 Changes of capacitance at several relative humidities.
(calcined diatomaceous earth)

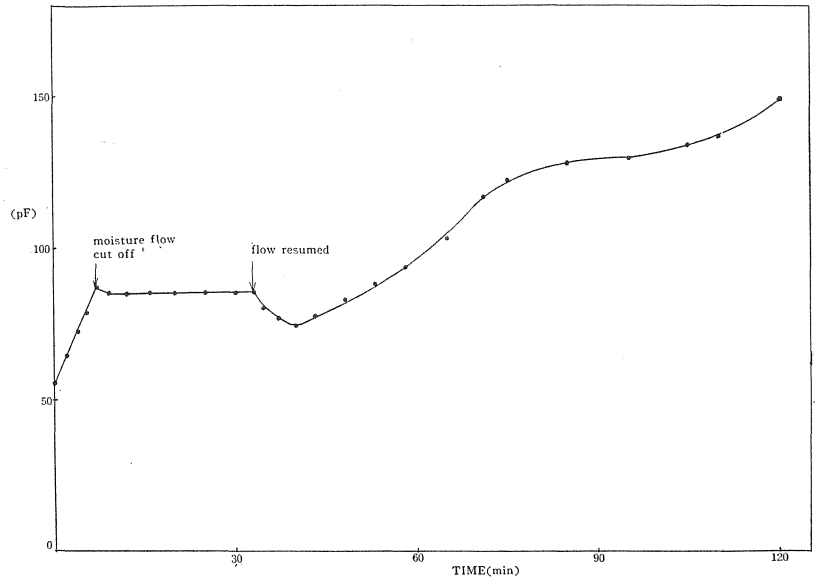

Fig. 21 Capacitance changes when moisture flow was cut off and set up again. (calcined diatomaceous earth)

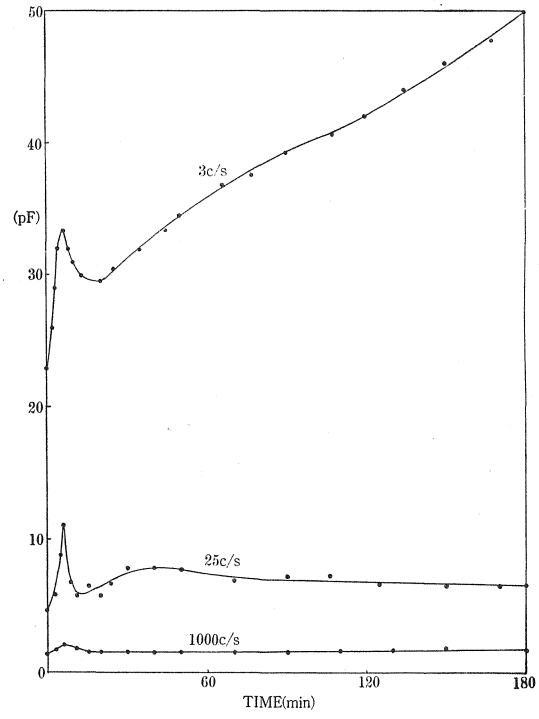

Fig. 22 Capacitance changes during moisture adsorption measured at the frequencies indicated. (filter paper)

the diameter of the leak cock is 1.5mm and 0.3mm. These show that the specimen adsorbs water very slowly when its rate of flow was diminished, but the height of the peak is independent of the rate. That is, the peak is not caused by the rapid flowing of moisture. The frequency dependence of the capacitance at the time of peak and at a fixed time of ascending after the minimum is shown by curves (a) and (b) in Fig. 19. The curve (b) in log-log plotting is nearly a straight line showing that the mechanism of the capacitance at that time must be due to the electrode polarization mentioned in the previous paper[5].

The curves in Fig. 20 show the changes of capacitance at different relative humidities. The time dependence of capacitance when the moisture flow was stopped at the time of peak of capacitance and resumed after about half an hour is shown in Fig. 21.

Filter paper

The slit between the electrodes on the filter paper was lmm wide and 22mm long.

(Case 2)

An example of the time dependence of the capacitance is shown in Fig. 22.

4. Conclusions

(1) The time effect on capacitance during adsorption of water is somewhat different according as the specimen is placed in a vacuum or dry air.

(2) The adsorption of water should not be regarded to end at the time of initial maximum capacitance but to proceed still further after that.

(3) A peak of capacitance appears also when a specimen with adsorbed water is dried very slowly.

(4) When a specimen placed in a vacuum adsorbs moisture, the surface dc conductivity reaches a peak more quickly than the capacitance, and the mechanism of the capacitance of the water during adsorption seems to be different from that of the dc conductivity.

(5) If a NMR experimet is conducted in parallel with the dielectric measurement, a more accurate conclusion may be obtained about the changes of structure of water during adsorption.

References

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Sci. Rep. Kanazawa Univ. **8** (1963) 279.
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