The Changes in Dielectric Properties of Water during Adsorption by Solids II.

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The Changes in Dielectric Properties of Water during Adsorption by Solids II*

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1. Introduction

In a previous paper[1], we dealt with the changes in dielectric properties of water during adsorption by solids at room temperature. The adsorbed water on a variety of solids, such as alumina and silica gels, and on saccharose has been reported to exhibit pronounced dielectric losses down to a temperature of about $-90°C$[2][3]. Therefore, it is interesting to extend the previous study to the case below the temperature of 0 °C. In the previous study moist air of one atmospheric pressure at desired relative humidity was transferred to the specimen. In the course of the present experiment, it was observed that the dielectric properties of water during adsorption was influenced by the composition of air and water vapour in the moist air. The result for the moist air with various mixing ratios of air and water vapour is reported in this paper. The time effects in dielectric properties of water during adsorption by evaporated films of salts of various kinds were reported by Weaver[4]. We tried to use films of some substances crystalized on glass plate or in porous calcined diatomaceous earth from their solutions.

2. Experimental Procedure and Specimens

The dielectric measurements were carried out with the apparatus described previously[1] at frequencies as low as 3 c/s, because the time effect during adsorption of water was especially conspicuous at very low frequencies. Other experimental procedures were also generally similar to the case of the previous work. The specimens used as adsorbents for this investigation and their electrodes for dielectric measurements were as follows.

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* A part of the results described in this paper was reported as a Short Note in the J. Phys. Soc. Japan 24 (1968)1174.

Soda lime glass

Mica

Two aluminum foils seperated by a slit were attached on the surface with water and dried.

Calcined diatomaceous earth

A coating of silver paste was given to each surface of the plate and fired.

Film of NaCl or $NaNO_2$

A plate of calcined diatomaceous earth attached with the electrodes was immersed in a 5% solution of NaCl and dried.
A 5% solution of $NaNO_2$ was put on the part of a slit of a soda lime glass plate attached with the electrodes and dried.

3. Results and Discussion

(a) *Temperature dependence of the changes in dielectric properties of water during adsorption*

The curves in Fig. 1 show the changes of capacitance when moist air of 53% relative humidity at 25°C was transferred to a soda lime glass plate (the slit was about 0.15 mm wide and 350 mm long) placed in a vacuum at the temperature indicated. The temperature dependence of the initial peaks of these curves of capacitance is shown in Fig. 2. It decreases with lowering of the temperature of the adsorbent below 0°C, and disappers at about −40°C. So the orientational freedom of water molecules, which was considered hitherto to explain the initial peak of capacitance[1], might not be motivated at low temperature such as −40°C. Obviously the dielectric dispersion showing the initial peak must be different from that exhibits dielectric loss down to a temperature of about −90°C discovered by Freymann[2].

Similar phenomena to the above were obtained with NaCl film crystalized in porous calcined diatomaceous earth plate (2.5 mm × 25 mm × 18 mm) as shown in Fig. 3, Fig. 4 and Fig. 5. Fig. 3 is of the case above the room temperature 25°C, and Fig. 4 is of the case below it. Fig. 5 shows the temperature dependence of the initial peaks of these curves of capaitance. The decrease of the initial peak with ascending of the temperature from the room temperature may be due to the lowering of the relative humidity of the moist air.

(b) *The effect of a variation of the composition of moist air on the dielectric properties of water during adsorption.*

The relative content of air in the moist air which was transferred to a specimen placed in a vacuum was varied by mixing of air and saturated water vapour at the pressure 17 mm Hg.

The curves given in Fig. 6 show the changes of capacitance for a soda lime glass at the total pressures of the moist air indicated (at 28°C). It is found that the initial peak of the capacitance decreases with the decreasing of the relative content of air in

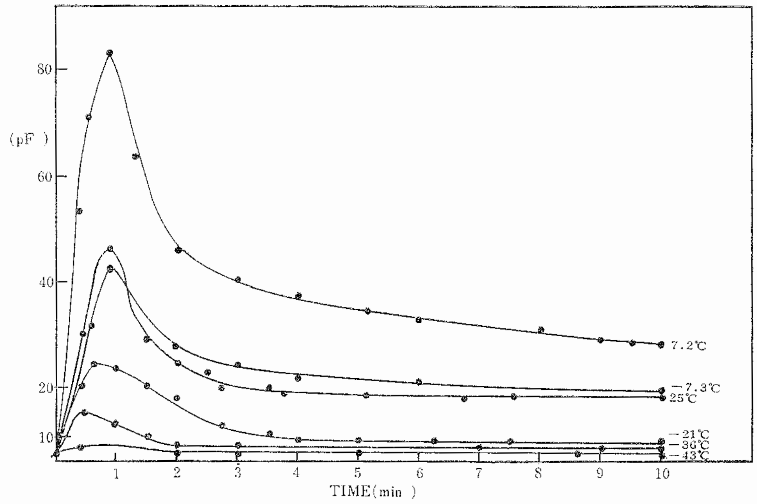

Fig. 1 Capacitance changes during moisture adsorption at the temperatures indicated, measured at the frequency 3c/s. (soda lime glass)

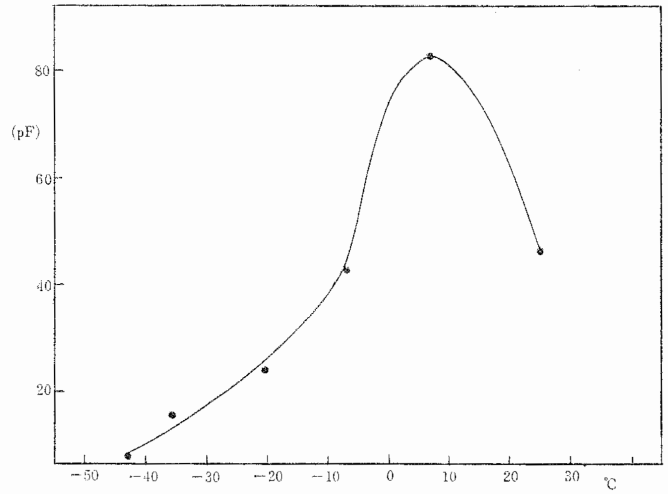

Fig. 2 Temperature dependence of the initial peaks of the capacitance shown in Fig. 1

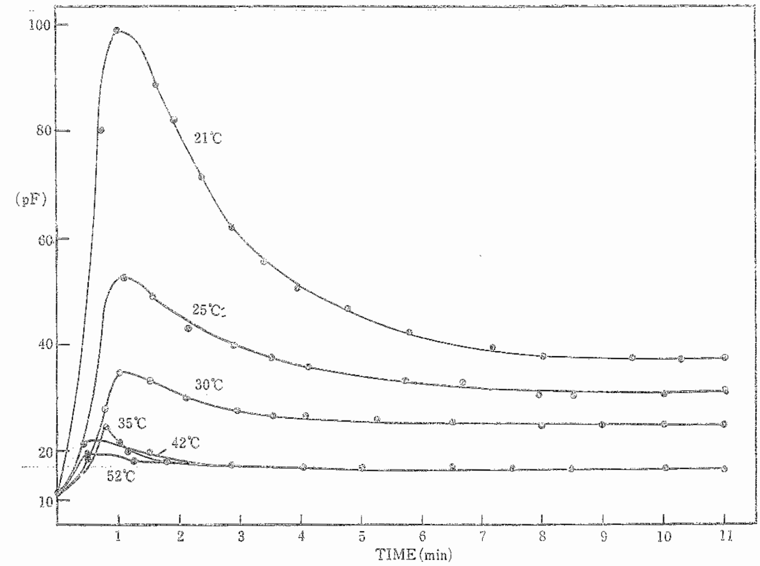

Fig. 3 Capacitance changes during moisture adsorption at the temperatures indicated (above the room temperature 25°C), measured at the frequency 3c/s. (NaCl film in porous calcined diatomaceous earth)

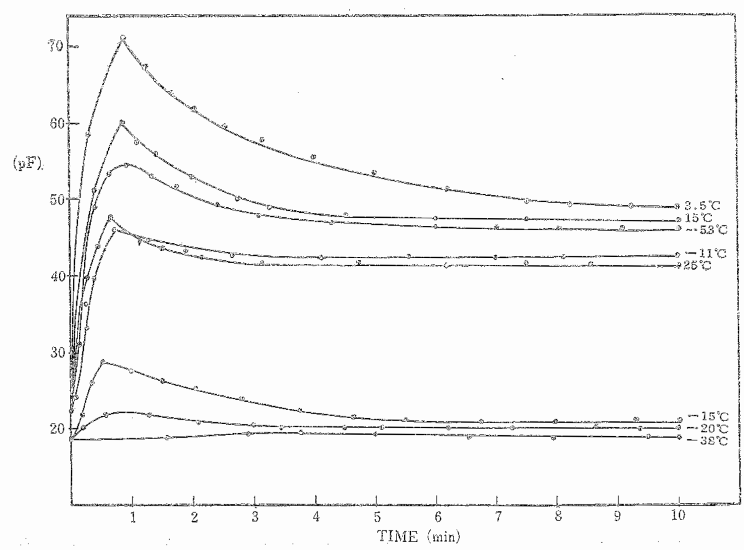

Fig. 4 Capacitance changes during moisture adsorption at the temperatures indicated (below the room temperature 25°C), measured at the frequency 3 c/s. (NaCl film in porous calcined diatomaceous earth)

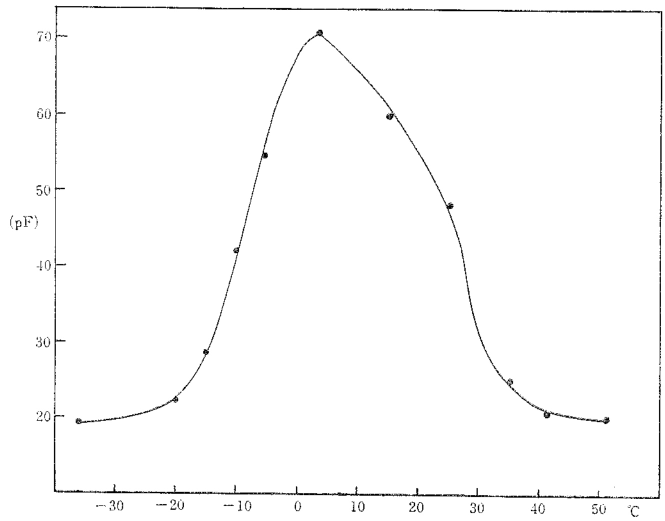

Fig. 5 Temperature dependence of the initial peaks of the capacitance shown in Fig. 3 and Fig. 4.

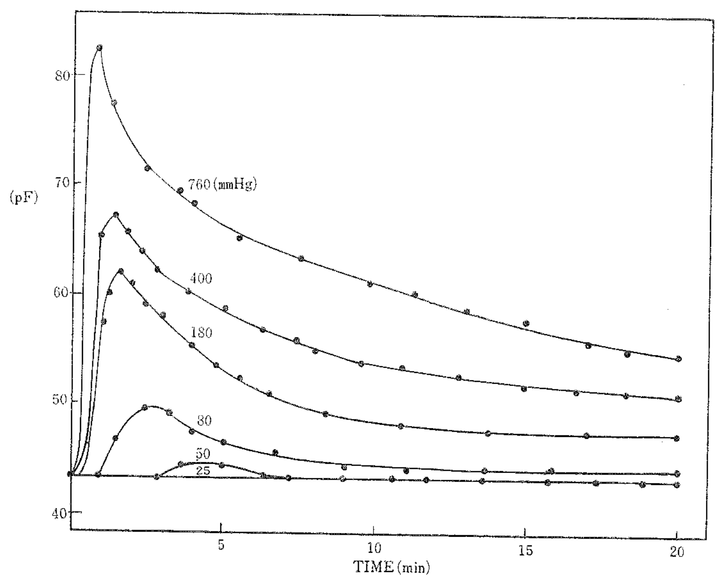

Fig. 6 The effect of a variation of the composition of moist air at the temperature 28°C, measured at the frequency 3 c/s. (soda lime glass) Figures indicated are total pressures (mm Hg) of moist air obtained by adding various air pressures to constant water vapour pressure 17 mm Hg. Similar figures are indicated in Fig. 7, Fig. 8, Fig. 9 and Fig. 10.

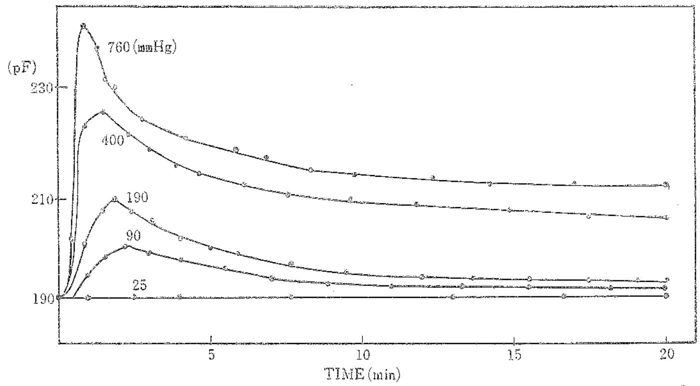

Fig. 7 The effect of a variation of the composition of moist air at the temperature 29°C, measured at the frequency 3 c/s. (mica)

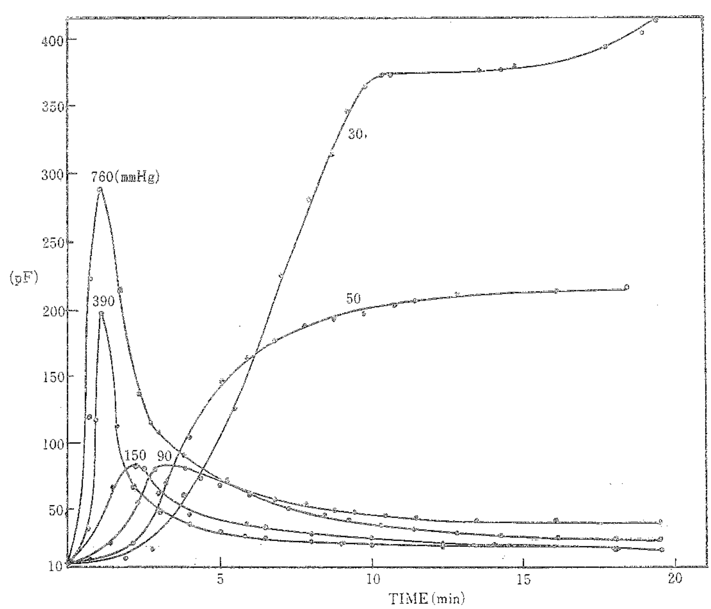

Fig. 8 The effect of a variation of the compositin of moist air at the temperature 29°C, measured at the frequency 3 c/s. ($NaNO_2$, film on soda lime glass plate)

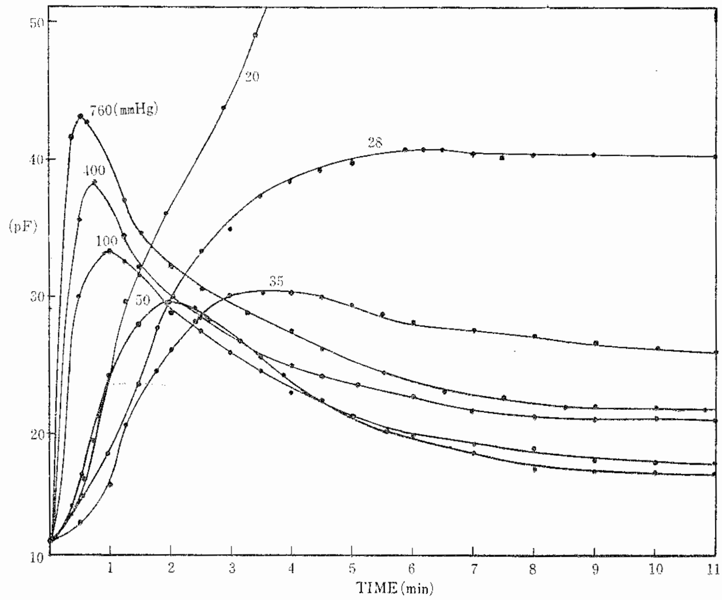

Fig. 9 The effect of a variation of the composition of moist air at the temperature 29°C, measured at the fuquency 3 c/s. (calcined diatomaceous earth)

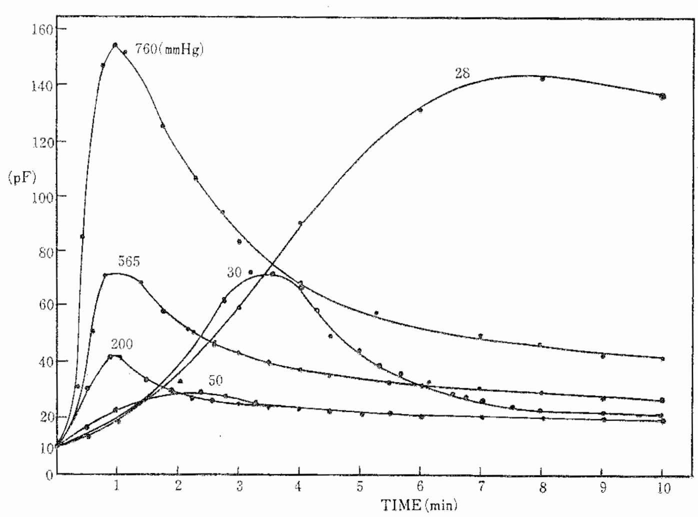

Fig. 10 The effect of a variation of the composition of moist air at the temperature 29°C, measured at the frequency 3 c/s.
(NaCl film in porous calcined diatomaceous earth)

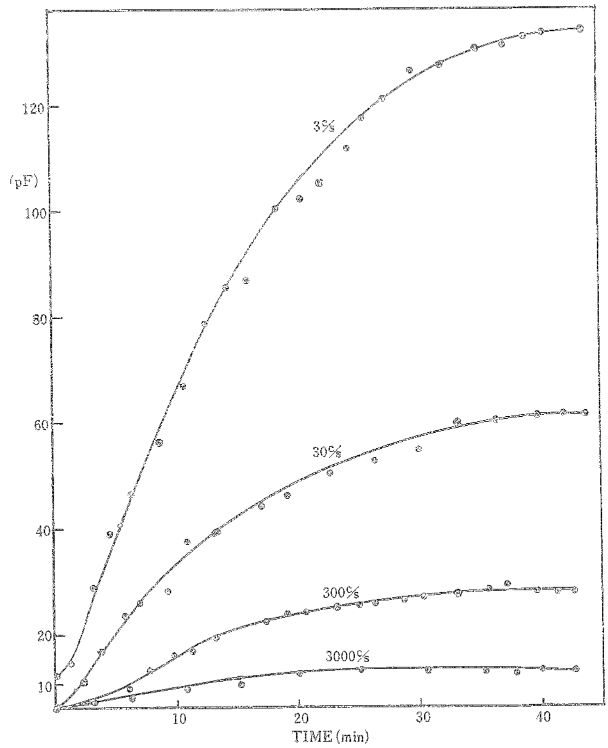

Fig. 11 Frequency dependence of the capacitane during moisture adsorption at the temperature 18°C. The total pressure of moist air is 28mm Hg obtained by adding air pressure 11mm Hg to water vapour pressure 17mm Hg.
(NaCl film in porous calcined diatomaceous earth)

the moist air. For the appearance of the initial peak some amount of air must be contained in the moisture. This seems to be perhaps due to the lack of active sites on the surface of the speimen on account of the small pressure of air. Furthermore the position of the intial peak shifts to long time side with the decreasing of the total pressure of the moist air. These facts were seen similarly for mica plate (the slit was about 0.08 mm wide and 330 mm long) as shown in Fig. 7. When $NaNO_2$ film on a soda lime glass plate, prepared after the manner as described in Section 2 was used, the effect of the variation of composition of moist air is somewhat complicated as shown in Fig. 8. That is, the inital peak of the capacitance decreases to a certain value with the decreasing of the pressure of air, and begins to increase markedly forming a broad maximum at very small peressure of air. Similar properties as for a $NaNO_2$ film are seen also for a plate of calcined diatomaceous earth and for a NaCl film crystalized in it as shown in Fig. 9 and Fig. 10 respectively. In these cases the initial peak of capacitance appears even at very small pressure of air contrary to the cases of soda lime glass plate and mica plate. This fact may be explained by the existence of more active sites on the surface of the former than on the latter.

For the reason why the capacitance increase abnormally at very small pressure of air we could not obtain the conclusion, but speculated as follows.

The large capacitance seems to be due to the electrode polarization described in a previous paper[5], on the assumption that the electrode polarization increases as the pressure of air decreases, or the provision of oxygen does. We found a conspicuous low frequency dielectric dispersion for a NaCl film in porous calcined diatomaceous earth at very small pressure of air (11 mm Hg) as shown in Fig. 11 which may be attributed to the electrode polarization.

4. Conclusions

The initial peak of the capacitance of water during adsorption decreases with the lowering of the temperature of the adsorbent below 0 °C, and disappears at about −40°C in some cases.

It decreases also with the decreasing of the relative content of air in the moist air for soda lime glass or mica, but for calcined diatomaceous earth plate, $NaNO_2$ film or NaCl film it increases at very small pressure of air contained in the moist air.

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