

Dielectric Behavior of water Adsorbed on Solid Surfaces at Very Low Frequencies (II)

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1. Introduction

In a previous paper⁽¹⁾ we reported the conspicuous dielectric dispersion, at very low frequencies, of water adsorbed on glass and mica surfaces, and attributed it to electrode polarization mentioned by Johnson and Cole⁽²⁾, on the ground that the dielectric dispersion decreased sharply as the distance between electrodes increased. According to the theory of Johnson and Cole the observed dielectric constant ϵ_{app} of a substance of large dc conductance is given by

$$\epsilon_{app} = \epsilon + (Z_o \sin n\pi/2)^{-(n+1)} G^2 / C_o,$$

where the ϵ is true dielectric constant of the specimen, G is the conductance, C_o is the geometrical capacity of the condenser, ω is $2\pi \times$ frequency, and Z_o is defined by the electrode impedance Z_{ei} as $Z_{ei} = Z_o(i\omega)^{-n}$. The exponent n is determined experimentally in each case and has the value 0.5 for solid formic acid and 1 for liquid formic acid. From this relation we know that the part of the capacity due to electrode polarization varies as G^2 and therefore inversely proportional to the square of the distance between the electrodes approximately. And we found a remarkable effect of distance between electrodes as was reported in the previous paper. In this paper the dependence of the capacity upon frequency which is expected from Johnson-Cole theory will be described. Furthermore it will be shown that the dielectric dispersion of water adsorbed on triglycine sulfate, $BaTiO_3$, calcined diatomaceous earth, and filter paper is partly due to electrode polarization.

2. Experimental Results and Discussion

Soda lime glass

Fig. 1 shows the log-log plots of the frequency dependence of the capacity of soda lime glass surface at 74%, 82% and 93% relative humidities. Two aluminum

foils (6.6μ in thickness) mounted on the surface and separated by a slit (0.32 mm wide and 75 mm long) were used as electrodes. The adhesive was water. It is noticed that the loci are straight lines in the lower frequency region.

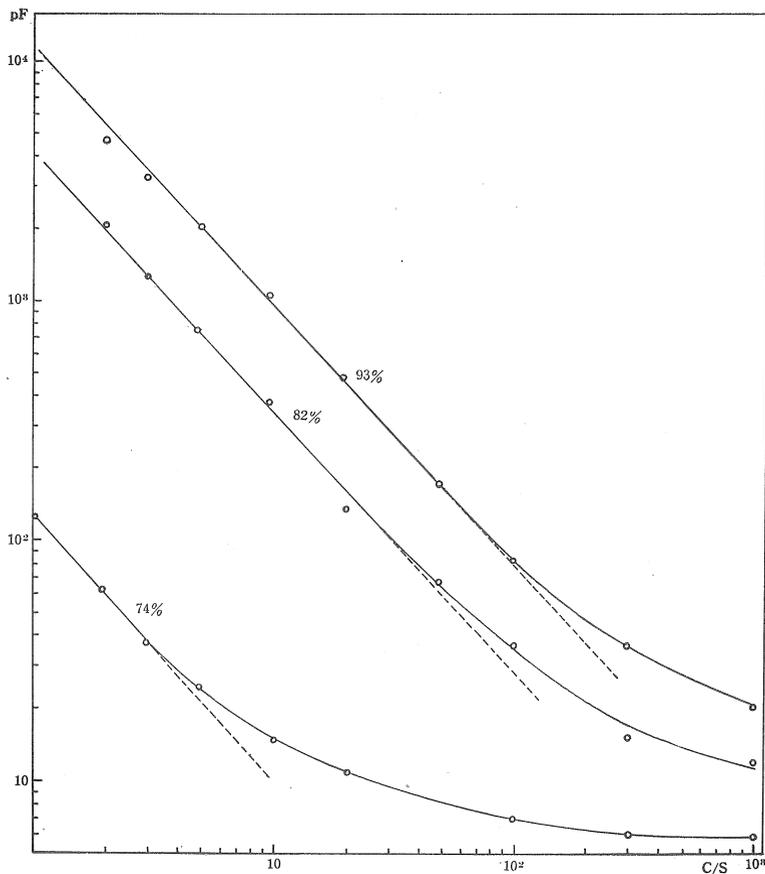


Fig. 1. The frequency dependence of the capacity of soda lime glass at various relative humidities (9°C).

Then we know that the dielectric constant varies nearly as $\epsilon^{-(n+1)}$ and n has the small value even at 93% relative humidity. From this also we may infer that the dielectric dispersion in the lower frequency region is to be attributed to electrode polarization. But we know that with frequencies higher than about 100 c/s other kinds of polarization such as orientational polarization of water molecules must have some contribution, because the loci deviate from straight lines. Fig. 2 shows the effect of the width of slit at 93% relative humidity, being a log-log plotting of the data shown in Fig. 8 of the previous paper⁽¹⁾. The straight lines have nearly equal slopes irrespective of the difference of the width of slit. It shows that the exponent n has the same value when the thickness of adsorbed water is equal.

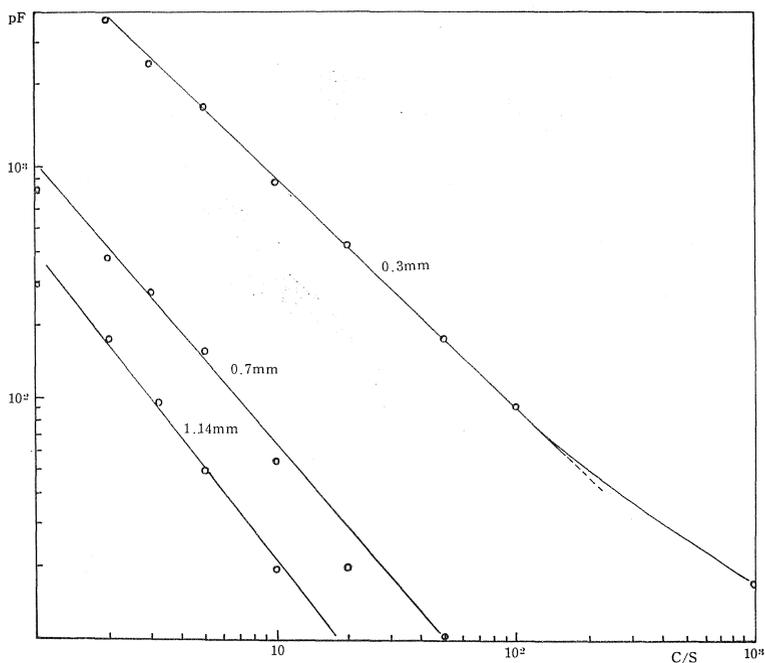


Fig. 2 The effect of the width of slit.

Triglycine sulfate

Triglycine sulfate is a ferroelectric which is soluble in water and shows a conspicuous dielectric dispersion at low frequencies as we reported in a previous paper⁽³⁾. The result given in the paper was obtained at 17% relative humidity and was seemed to be free from effects of humidity. But we found that at higher relative humidities the dispersion increased markedly. To find the origin we examined dielectrically the properties of water adsorbed on the surface of a triglycine sulfate crystal by the same method as in the case of soda lime glass. Fig. 3 shows the log-log plots of the frequency dependence of the capacity of c plane surface of triglycine sulfate at various relative humidities. Two aluminum foils attached on the surface with grease and separated by a slit (10 mm wide and 13 mm long) were used as electrodes. The loci in the lower frequency region are straight lines and so the dielectric dispersion may also be attributed to electrode polarization. The fact that the dispersion was noticeable with large a distance between the electrodes as 10 mm must be due to the large conductance of the crystal surface caused by the substance dissolved in the water film. There seems to be no other explanation. Fig. 4 shows the log-log plots of the frequency dependence of capacity of b-cut plate ($50 \text{ mm}^2 \times 1.93 \text{ mm}$) of a triglycine sulfate crystal at various relative humidities. Two aluminum foils attached with grease to the both surfaces were used as electrodes. The dielectric dispersion at zero humidity seems to be due to the triglycine sulfate itself. But at the higher relative humidities the dispersion due to the water adsorbed on the side surface of the crystal must be added to that of the crystal itself.

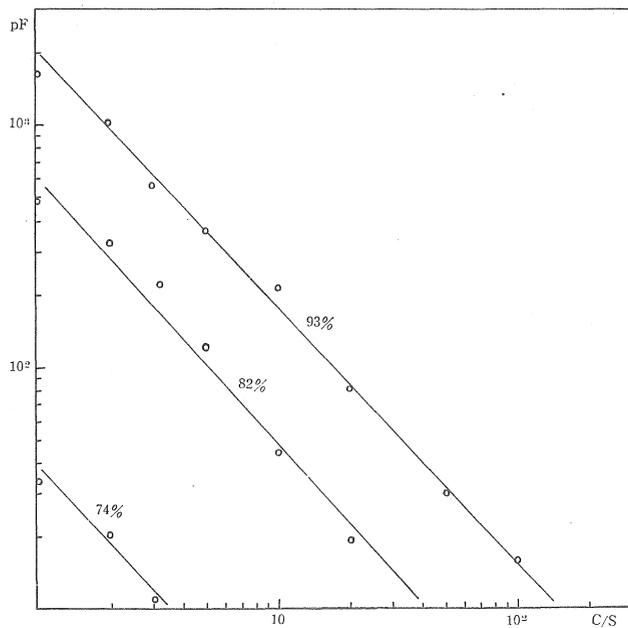


Fig. 3. The frequency dependence of the capacity of triglycine sulfate surface (C plane) at various relative humidities (12.5°C).

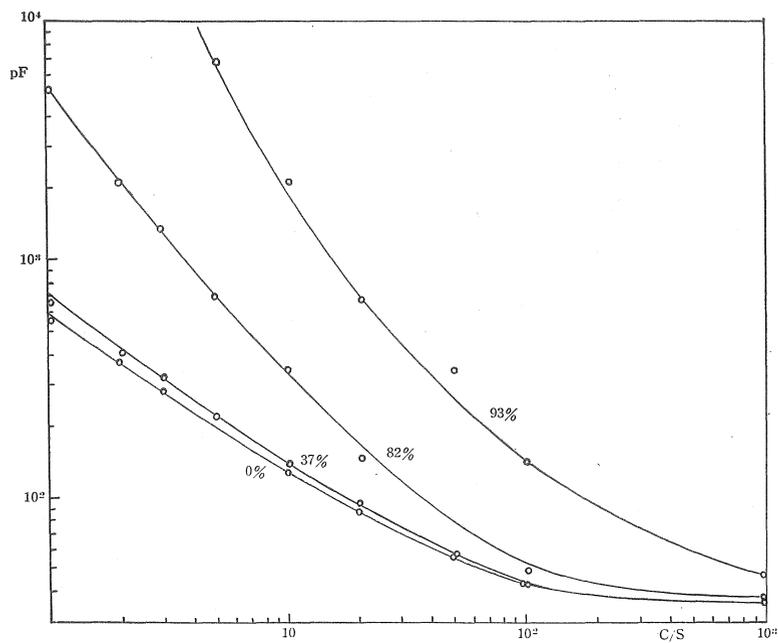


Fig. 4. The frequency dependence of the capacity of triglycine sulfate (b-cut plate) at various relative humidities (10°C).

BaTiO₃

The dielectric effect of water adsorbed on ceramic BaTiO₃ was reported by Marutake⁽⁴⁾. Fig. 5 shows the log-log plots of the frequency dependence of the capacity of ceramic BaTiO₃ plate (70 mm² × 1.75 mm) at various relative humidities. Silver paste painted on both surfaces of the plate served as electrodes. The dielectric dispersion is absent at zero humidity, but it appears as the relative humidity increases, and the loci at lower frequencies approach straight lines.

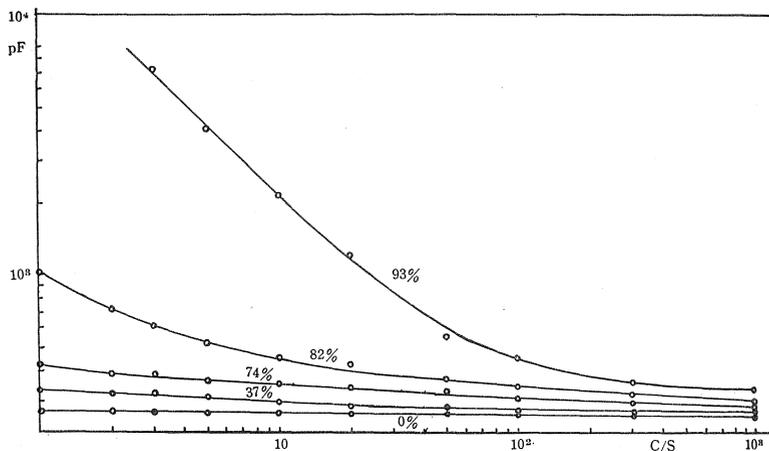


Fig. 5. The frequency dependence of the capacity of ceramic BaTiO₃ at various relative humidities (8°C).

Therefore the dispersion at lower frequencies may be attributed to electrode polarization. But since coating the side surface of the specimen with vaseline did not change the dispersion significantly we know that the electrode polarization is caused by the water adsorbed on the internal surfaces of the porous specimen. At higher frequencies other polarizations will contribute effectively also. For example there may be orientational polarization of water molecules and the effect mentioned by Marutake⁽⁴⁾, which is the result of enveloping of minute crystals of the ceramic by water film. Single crystals of butterfly type of BaTiO₃ also show conspicuous dielectric dispersion at low frequencies in a humid atmosphere probably owing to the electrode polarization of the water adsorbed on the side surface of very thin crystals.

Calcined diatomaceous earth

As an example of very porous substances we used a plate of calcined diatomaceous earth (50mm² × 1.55mm). Silver paste painted on both surfaces served as electrodes. The result is shown in Fig. 6. Even at 74% relative humidity the dispersion is remarkable, and the linearity of the loci in the lower frequency region is evident. This seems to be due to the small contribution from the polarization of the calcined diatomaceous earth itself.

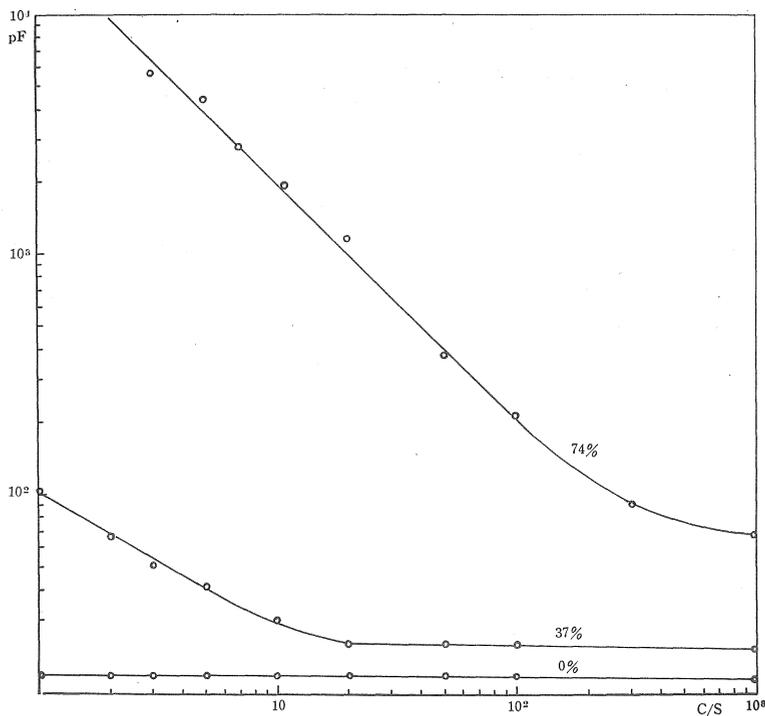


Fig. 6. The frequency dependence of the capacity of calcined diatomaceous earth at various humidities (10°C).

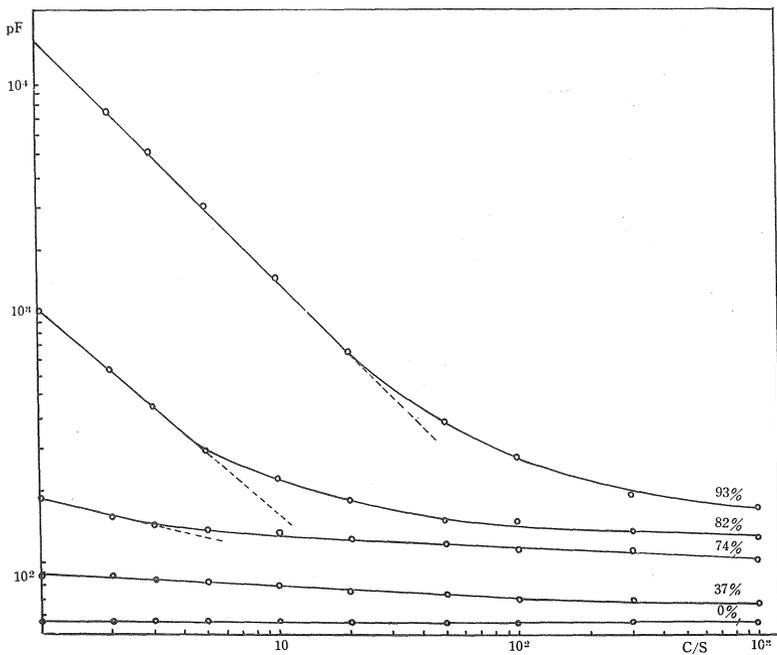


Fig. 7. The frequency dependence of the capacity of filter paper at various humidities (10°C).

Filter paper

Recently Tsuge and Wada⁽⁵⁾ reported the effect of adsorbed water on dielectric dispersion of cellulose at frequencies between 80 c/s—120 kc/s, and concluded that the low frequency dispersion of cellulose may be attributed to the rotational segmental motions of cellulose which start through the sorbed water molecules breaking the intra- and intermolecular hydrogen bonds. To make a comparative study we experimented with filter paper (0.2 mm thickness). Two circular brass electrodes (45 mm diameter) were employed in this case. The result is shown in Fig. 7. The loci are found to be linear in the region of frequencies lower than about 20 c/s at 93% relative humidity, showing the dielectric dispersion is due to electrode polarization, but in the higher frequency region other polarization probably contributes much more than electrode polarization.

References

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