BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1660—1663 (1973)

Dielectric Behavior of the Packing Bed of Alumina Granules with Adsorbed Water

Kaoru UMEYA and Takashi KANNO

Department of Chemical Engineering, Faculty of Engineering, Tohoku University, Aramaki-Aoba, Sendai 980

(Received December 16, 1971)

Dielectric behavior of the packing bed of alumina granules with various amounts of adsorbed water were determined in the frequency range 30 Hz—3 MHz. The dielectric relaxations characterized by a distribution in relaxation time were attributed to interfacial polarizations due to the adsorbed ions accumulated around the non-conductive points (*i.e.*, discontinuous points on conducting paths consisting of water films adsorbed on alumina granules). Some of the adsorbed ions were carried away to the electrodes through the points of contact between the water films adsorbed on granules adjacent to each other (*i.e.*, continuous conducting paths), giving rise to d.c. conductance and electrode polarization. When insulating sheets were inserted between the electrodes and surfaces of the packing bed, both the d.c. conductance and electrode polarization disappeared and another dielectric relaxation was observed. This was attributed to the interfacial polarization due to the ions accumulated at the interfaces between insulating sheets and water adsorbed on alumina granules.

Dielectric studies of water adsorbed on inorganic oxides have been made.[1,2] In order to study the mechanism of adsorption of water vapor and the nature of the adsorbed water, dielectric isotherms have frequently been determined for several frequencies.[3,4] With increasing amounts of adsorbate, contribution of adsorbed ions becomes significant and dielectric relaxations due to the interfacial polarizations are observed if measurements are made over a wide frequency range.[5-7] However, their mechanism has not been discussed in detail.

In the present study we discuss the mechanism of dielectric relaxations observed for the packing bed of alumina granules with adsorbed water. Since such a system is an assembly of individual granules, the dielectric properties as well as electrical conductance are affected by packing conditions of alumina granules. The results also change with the conditions of the contact of the specimen with electrode, since electrical conduction can be prevented if the contact is incomplete. For the sake of confirmation measurements were also made on a system in which electrical conduction was prevented by inserting polyethylene sheets (0.07 mm in thickness) between the electrodes and surfaces of the packing bed. The dependence of dielectric properties upon particle size was also studied.

Experimental

Alumina granules, spherical particles of porous alumina granules containing 10% silica "Neobead D" supplied from Mizusawa Chemical Engineering Co., Ltd. were used. Their specific surface area is 300 m^2/g. True density and packing density are 3.10 and 0.5—0.6 g/cm^3, respectively. Granules of two different particle size, *i.e.*, about 0.3 mm and 1.0 mm in diameter, were used.

A Type TR-1B Transformer Bridge from Ando Electric Company was employed for measurements of capacitance and conductance over the frequency range 30 Hz—3 MHz.

Results and Discussion

Dielectric Constant and Dielectric Loss. Dielectric constant ε' and dielectric loss ε'' measured on the packing bed of alumina granules with adsorbed water are plotted against frequency in Fig. 1, and compared with those of the specimen with insulating sheets inserted between the electrodes and surfaces of the packing bed. The dielectric loss of the specimen without insulators was obtained by subtracting the d.c. conductance.

In the lower frequency range the dielectric constant

---

[1] R. L. McIntosh, "Dielectric Behavior of Physically Adsorbed Gases", Marcel Dekker, Inc., New York (1966).

[2] S. S. Dukhin, "Surface and Colloid Science," Vol. 3, ed. by E. Matijevic, Wiley-Interscience, New York (1971), p. 83.

[3] M. G. Baldwin and J. C. Morrow, *J. Chem. Phys.*, **36**, 1591 (1962).

[4] N. K. Nair and J. M. Thorp, *Trans. Faraday Soc.*, **61**, 962, 975 (1965).

[5] P. G. Hall and G. K. Kouvarellis, *ibid.*, **64**, 1940 (1968).

[6] S. M. Nelson, H. H. Huang, and L. E. Sutton, *ibid.*, **65**, 225 (1969).

[7] E. McCafferty, V. Pravdic, and A. C. Zettlemoyer, *ibid.*, **66**, 1720 (1970).

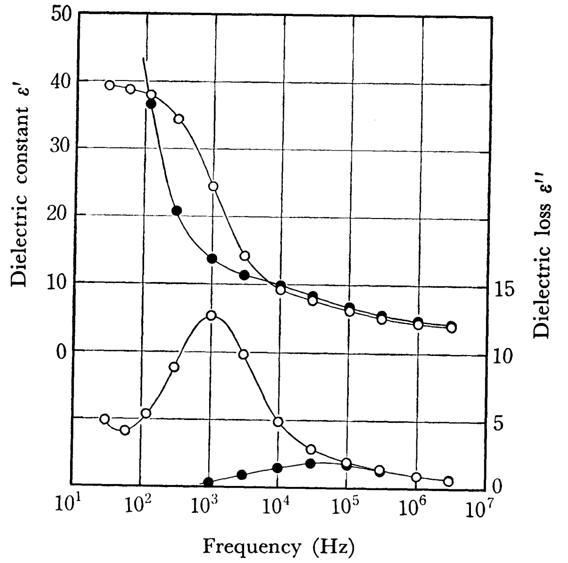

Fig. 1. Frequency dependence of dielectric constant and dielectric loss at 30 °C. Amount of water adsorbed: 200 mg/g. Particle diameter: 0.3 mm.
○: measured with insulating sheets.
●: measured without insulating sheets.

of the specimen with no insulating sheets increased rapidly with decreasing frequency. This can be attributed to the electrode polarization which arises from the electrolytic polarization of ions on electrode surfaces. In the same frequency range the dielectric constant of the specimen with insulating sheets had a tendency to reach a plateau with decreasing frequency accompanied by a distinct peak in the dielectric loss curve. This can be attributed to the dielectric relaxation due to the interfacial polarization which arises from the ions accumulated at the interfaces between insulating sheets and water adsorbed on alumina granules.

In a higher frequency range the dielectric constants of both specimens decreased gradually with increasing frequency. The dielectric dispersion can be attributed to the interfacial polarizations which arise from the adsorbed ions within the packing bed of alumina granules. A well-defined peak in the dielectric loss curve was observed for the specimen without insulating sheets, whereas in the case of that with insulators no distinct peak was found. It can be seen, however, that the dielectric loss curve of the specimen with insulating sheets almost coincides with that of the specimen without insulators in frequency range above 100 kHz.

Complex Plane Plots of ε' and ε''. The complex plane plots of ε' and ε'' measured on the specimen without insulators gave a circular-arc as shown in Fig. 2. Thus the complex dielectric constant of the packing bed of alumina granules with adsorbed water is represented approximately by the following equation:[8,9]

$$\varepsilon^* = \varepsilon_h + \frac{\varepsilon_l - \varepsilon_h}{1+(i\omega\tau)^\beta} + \frac{\kappa_l}{i\omega\varepsilon_v} \tag{1}$$

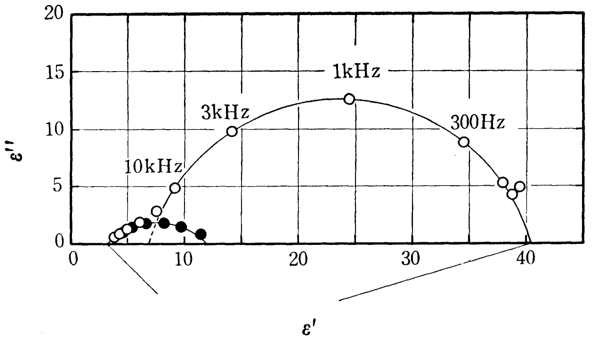

Fig. 2. Complex plane plots of ε' and ε''. Amount of water adsorbed: 200 mg/g. Particle diameter: 0.3 mm.
○: measured with insulating sheets.
●: measured without insulating sheets.

where ε_h and ε_l are the limiting dielectric constants at high and low frequencies, respectively; κ_l is the limiting conductivity at low frequency (*i.e.*, d.c. conductivity) subtracted in calculating the dielectric loss; $\omega(=2\pi f)$ measuring angular frequency, $\tau(=1/2\pi f_0)$ mean relaxation time, f and f_0 measuring frequency and relaxation frequency for which the dielectric loss is a maximum, respectively; β parameter for the distribution of relaxation times, and $\varepsilon_v = 8.8541 \times 10^{-14}$ F/cm and $i=\sqrt{-1}$.

In the case of the specimen with insulating sheets a large circular-arc corresponding to the relaxation in low frequencies was observed. Several plots in the high frequency range deviate from the ciruclar-arc and lie on that of the specimen without insulators. The tail appearing on the circular-arc reveals the presence of another dielectric relaxation in the high frequency range, which seems to be the same relaxation as that of the specimen without insulators. The complex dielectric constant of the specimen with insulating sheets, therefore, can be expressed by the following equation:

$$\varepsilon^* = \varepsilon_h + \frac{\varepsilon_i - \varepsilon_h}{1+(i\omega\tau_1)^\beta} + \frac{\varepsilon_l - \varepsilon_i}{1+(i\omega\tau_2)^\alpha} \tag{2}$$

where ε_h, ε_l and ε_i denote the values of limiting dielectric constants at high and low frequencies and at an intermediate plateau, respectively; τ_1 and τ_2 are the mean relaxation times of polarizations at high and low frequencies, respectively; β and α are parameters for the distribution of relaxation time of individual polarization.

Since the relaxations in high and low frequencies overlapped partially, no distinct corresponding circular-arcs were observed. The circular-arc in low frequencies (Fig. 2) might not represent the one corresponding to the relaxation in low frequencies precisely, but involves a part of relaxation in high frequencies.

The dielectric relaxations overlapping each other were separated into two individual ones. The circular-arc corresponding to the relaxation at high frequencies was first drawn with respect to that of the specimen without insulators (broken line, Fig. 3). From this the numerical values of the first and second terms of the right side in Eq. (2) were determined. The dielectric constants and dielectric losses calculated by

---

[8] T. Hanai, "Emulsion Science," ed. by P. Sherman, Academic Press, London and New York (1968), p. 354.

[9] K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 314 (1941).

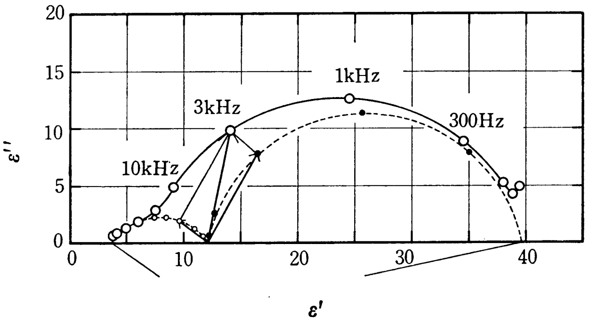

Fig. 3. Complex plane plots of ε' and ε'' separated into two individual circular-arcs (broken curve).

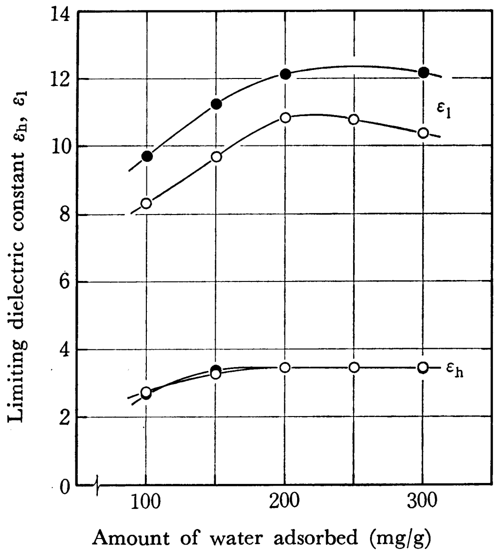

Fig. 4. Limiting dielectric constants ε_h, ε_l as a function of amount of adsorbed water. Particle diameter: 1.0(○), 0.3(●) mm.

use of this equation are plotted with open circles.

The dielectric constants of the relaxation in low frequencies can be obtained by adding the values equal to the dielectric decrements due to relaxation in high frequencies to those observed. The dielectric loss of relaxation in low frequencies can also be obtained by subtracting the values due to relaxation in high frequencies from those observed. The complex plane plots obtained by use of these values are shown by a broken line with full circles. These procedures can also be expressed in vector form (Fig. 3).

A similar behavior to that mentioned above was observed in different amounts of adsorbed water for both the specimens with and without insulating sheets.

For the specimen without insulators, dielectric measurements were also carried out on granules of about 1.0 mm in diameter. The experimental values of the parameters in Eq. (1) will be discussed in detail.

Limiting Dielectric Constants: The limiting dielectric constants at high and low frequencies ε_h and ε_l, respectively, are plotted against the amounts of adsorbed water in Fig. 4. The values of ε_h and ε_l increased first with increasing amount of adsorbed water, but for higher water content, the value of ε_l decreased with the increase of the amount of adsorbed water, and that of ε_h remained almost constant.

Murphy and Lowry proposed a mechanism of dielectric polarization for "Interstitial Conducting Systems."[10] The electrical conduction of moistened dielectrics takes place through interstitial conducting paths of water film containing ions in a certain concentration. The ions near the surface are adsorbed so strongly that they cannot be detached under the effect of an external field but can be displaced along the surface, giving rise to polarization.

Miles and Robertson,[11] and Schwarz[12] extended the Wagner theory[13] to a dispersed system of spherical particles with electrical double layer.

However, these theories cannot interpret the decrease of the values of ε_l observed in a large amount of adsorbed water. The dielectric relaxations observed in this study might be attributed to the interfacial polarization which arises from the ions accumulated around the non-conductive gaps between water films adsorbed on the granules adjacent to each other, *i.e.*, discontinuous points on conducting paths. At a higher water content these gaps are bridged with water films and the ions accumulated may be carried away to the electrode through the points of contact, giving rise to d.c. conductance and electrode polarization. Thus in higher water contents the values of ε_l decrease with increasing amount of adsorbed water.

The values of ε_l also change with particle size as shown in Fig. 4. This may be interpreted by the difference in number of non-conductive points. The packing bed of small granules may be expected to have a large number of non-conductive points, resulting in an increase in the value of ε_l.

The values of ε_h corresponding to polarization due to the ions strongly adsorbed were not affected by particle size. This is understandable since the specific surface area of the granules do not change with the difference in particle size as they have a porous structure.

Mean Relaxation Frequency: The mean relaxation frequency f_0 is plotted in Fig. 5 as a function of the

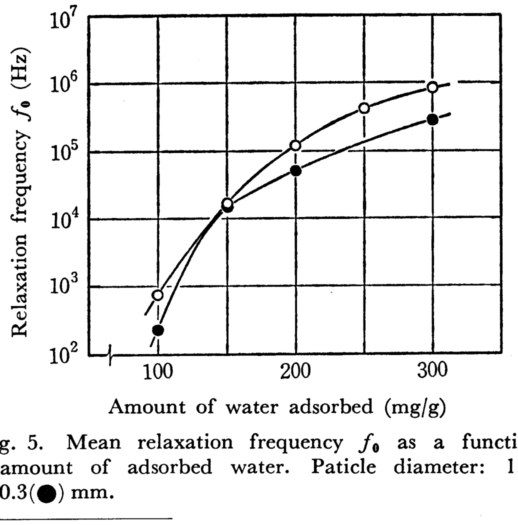

Fig. 5. Mean relaxation frequency f_0 as a function of amount of adsorbed water. Paticle diameter: 1.0(○), 0.3(●) mm.

---

[10] E. L. Murphy and H. H. Lowry, *J. Phys. Chem.*, **34**, 598 (1930).

[11] J. B. Miles and H. R. Robertson, *Phys. Rev.*, **40**, 583 (1932).

[12] G. Schwarz, *J. Phys. Chem.*, **66**, 2636 (1962).

[13] K. W. Wagner, *Arch. Elektrotech.*, **2**, 371 (1914).

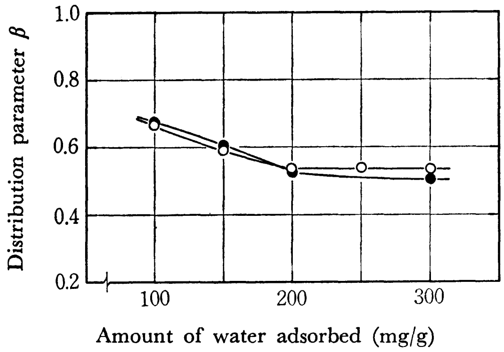

Fig. 6. Distribution parameter β as a function of amount of adsorbed water. Particle diameter: 1.0(○), 0.3(●) mm.

amount of water adsorbed. The increase in the value of f_0 with increasing adsorbate can be attributed to the formation of weakly adsorbed layers. The decrease in the rate of increase of f_0 in a higher water content can be attributed to the saturation or decrease in the polarization described above.

The mean relaxation frequency increases with the increase of particle size. This can be interpreted in terms of the difference in geometrical surface area as well as the difference in number of non-conductive points. As the particle size increases geometrical surface area decreases, and the effect of surface becomes smaller for the same water content.

Distribution Parameter: The distribution parameter β is plotted in Fig. 6 as a function of the amount of adsorbate. Decrease in the value of β at low water content can be interpreted in terms of the increase in polarization with a small relaxation time. For water content above 200 mg/g the value of β remained almost constant irrespective of the amount of adsorbate. This is attributed to the saturation or decrease in polarization. The value of β was not affected by particle size (Fig. 6).

Table 1. Values of ε_h, ε_i, ε_l, f_{01}, f_{02}, β and α in various amounts of water adsorbed on alumina

Amount adsorbed (mg/g)	ε_h	ε_i	ε_l	f_{01} (kHz)	f_{02} (kHz)	β	α
100	2.9	10.1	—	0.56	—	0.733	—
200	3.6	12.1	39.8	16.8	1.1	0.628	0.872
300	3.5	11.5	38.7	224	8.5	0.600	0.922

The results observed for the specimen with insulating sheets are shown in Table 1.

The limiting dielectric constants ε_h and ε_i, the mean relaxation frequency f_{01} and the distribution parameter β for the specimen with insulating sheets were almost coincident with those of the specimen without insulators. The limiting dielectric constant at low frequency ε_l and the mean relaxation frequency f_{02} can be explained by means of the Maxwell theory of a stratified model.[8] The distribution in relaxation time can be attributed to the heterogeneity in limiting conductivity at low frequency κ_l observed for the specimen without insulators.