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The Effect of Deuterium Exchange of Silica Gel on Dielectric Relaxation*1

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In a previous paper,[1] a study was made on the influence of adsorbed water and heat treatment of silica gel on its dielectirc properties with respect to surface structure. Two dielectric relaxations (Dispersion I and II) and one anomaly (Anomaly III) were found and interpreted as having close relation with the adsorbed water, the hydrogen-bond chain of surface silanol groups and free silanol groups, respectively.

This interpretation seems to have further experimental support by the dielectric investigation of deuterated silica gel shown in this paper.

Experimental

The material and the experimental procedure were the same as described.[1] The deuterium exchange of silica gel was carried out by repeating adsorption and desorption of heavy water of 99.8% purity 6 times.[2] The concentration of deuterium with respect to the original hydrogen content was estimated to be roughly 60 to 70% by assuming this concentration approximately equal to the ratio of the intensity decrease of the OH stretching vibration band at 3750 cm^{-1} to the original intensity.

Results and Discussion

The curves *a*, *b*, *c* and *d* in Fig. 1 show the relation of the values of tan δ at 1 kHz to the temperature of deuterated silica gel having 0.50 and 2.7 mmol D_2O per 1 g silica gel and heat-treated at 200°C and 500°C, respectively. The behavior of these curves seems very similar to the dotted curves *a'*, *b'*, *c'* and *d'* of ordinary silica gel having 0.56 and 2.9 mmol H_2O per 1 g silica gel (equal to 1.0 and 5.3 wt% H_2O respectively) and heat-treated at 200°C and 500°C, respectively. The tan δ anomalies of curves *a* and *b* can be considered as the dielectric relaxations (Dispersion I' and II') by the Cole-Cole arc plot calculated from these curves partly shown in Fig. 2. The shape and size of these arcs are almost similar to those of Dispersion I and II of light-water silica gel as also shown in Fig. 2. Disappearance of the higher temperature relaxation (Dispersion I') by

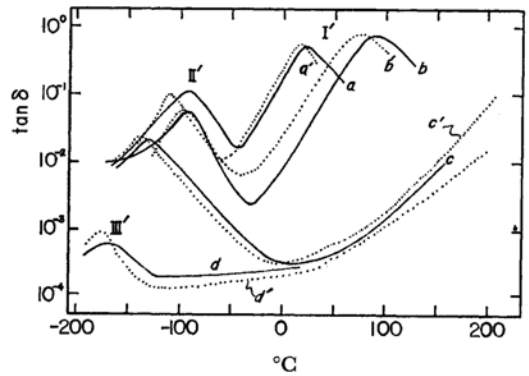

Fig. 1. The curves of tan δ *versus* temperature of deuterated and ordinary silica gel.
a and *a'*: 2.7 and 2.9 mmol D_2O and H_2O/1 g silica gel at 170°C, respectively. *b* and *b'*: 0.50 and 0.56 mmol D_2O and H_2O/1 g silica gel, respectively. *c* and *c'*: heat treatment at 200°C. *d* and *d'*: heat treatment at 500°C.

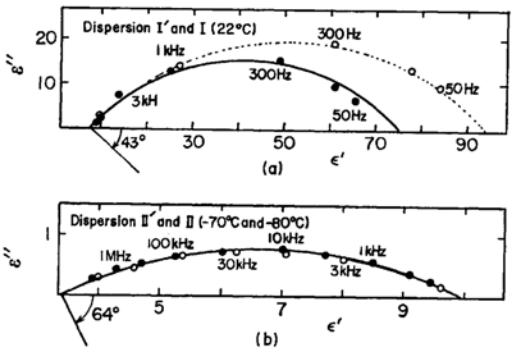

Fig. 2. Cole-Cole are plots of Dispersion I', I, II' and II of deuterated and ordinary silica gel.
(a) ●: Dispersion I' at 22°C. ○: Dispersion I at 22°C.
(b) ●: Dispersion II' at −70°C. ○: Dispersion II at −80°C.

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1) S. Kondo and M. Muroya, This Bulletin, **42**, 1165 (1969).

2) A. Soffer and M. Folman, *Trans. Faraday Soc.*, **62**, 3559 (1966); J. B. Peri and R. B. Hannan, *J. Phys. Chem.*, **64**, 1526 (1960).

heating at 200°C (see curve *c* in Fig. 1) shows that this relaxation originates in heavy water adsorbed, as seen analogously in the thermal behavior of Dispersion I. A similar discussion on Dispersion II′ leads to the view point that Dispersion II′ is caused by the shift of Dispersion II by deuterium exchange. The curves of ε' and ε'' versus frequency of Dispersion I′ and II′ show that these dispersions seem to be the same type as Dispersion I and II respectively. The tan δ anomaly (Anomaly III′)

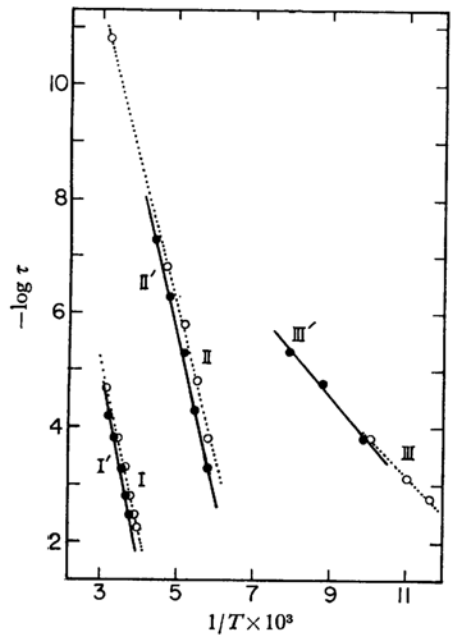

Fig. 3. The relationship of reciprocal temperature to log τ of Dispersion I′, I, II′ and II and log $\frac{1}{2}\pi f$ of Anomaly III′ and III.
●: D_2O exchange ○: H_2O-silica gel

in curve *d* of Fig. 1 can be interpreted also as the shift of Anomaly III.

The full lines of Fig. 3 show the relation of the relaxation times, log τ, of Dispersion I′ and II′ and the log $\frac{1}{2}\pi f$ of Anomaly III′, in which f is the frequency of ε'' maxima obtained from the ε''-temperature relation, to the reciprocal temperature $(1/T)$. The corresponding lines of light-water silica gel as shown by dotted lines in this figure are very close to the full lines. The activation energies ΔE and constants τ_0 of Dispersion I′, II′ and Anomaly III′ obtained from Fig. 3, together with those of Dispersion I, II and Anomaly III, are listed in Table 1. In reference to the effect of

Table 1. Activation energy ΔE and constant τ_0 of dispersion I′, I, II′, II, anomaly III′ and III of deuterated and ordinary silica gel

Dispersion	Water content or heat-treatment temperature	ΔE (kcal/mol)	τ_0 (sec)
I′	2.7 mmol D_2O/1 g SiO_2	14.8±0.2	3.3×10^{-16}
I	2.9 mmol H_2O/1 g SiO_2	13.5±0.2	2.8×10^{-19}
II′	0.50 mmol D_2O/1 g SiO_2	12.3±0.2	5.0×10^{-19}
II	0.56 mmol H_2O/1 g SiO_2	11.4±0.2	2.0×10^{-18}
III′	Heat-treated at 500°C	3.1±0.5	5×10^{-11}
III		3.0±0.5	2×10^{-10}

the amount of adsorbed water on the values of ΔE and τ_0 examined in a previous work,[1] the small difference of mol% of adsorbed water between heavy and light-water would not give an appreciable change in the values of ΔE and τ_0 of dielectric relaxation. In this table, the value of ΔE increases and τ_0 decreases by deuterium exchange. Further investigation is necessary for the more detailed discussion on the values of ΔE and τ_0 of these relaxation phenomena of deuterated silica gel.