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The state of water molecules sorbed on Al_2O_3 by dielectric measurements

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Résumé.

La constante diélectrique (ϵ) et les pertes diélectriques ($\text{tg } \delta$) d'un système $\gamma - \text{Al}_2\text{O}_3$ ont été mesurées entre $+ 25^\circ \text{C}$ et $- 60^\circ \text{C}$, aux fréquences de 100 kHz, 1000 kHz, et 7000 kHz et pour des concentrations en eau (a) allant jusqu'à 100 mg/g. Les courbes $\epsilon - a$ et $\text{tg } \delta - a$ (isothermes) présentent deux points d'inflexion. Le premier point d'inflexion est, par opposition au second, indépendant de la température et de la fréquence dans nos conditions expérimentales. Il en est de même pour la première partie des trois segments linéaires d'isothermes.

Pour des concentrations supérieures à 48 mg/g, la pente des isothermes de ϵ et $\text{tg } \delta$ est très faible entre $- 40^\circ$ et $- 60^\circ \text{C}$. Dans cette région, ni ϵ ni $\text{tg } \delta$ ne sont réversibles après refroidissement à $- 60^\circ \text{C}$. On obtient dans les diagrammes $\epsilon - T$ et $\text{tg } \delta - T$ des « courbes d'hystérèse ».

D'après Frenkel, une molécule se trouvant en équilibre d'adsorption reste à la surface pendant le temps d'adsorption τ . Pour τ nous avons la relation $\tau = \tau_0^{Q/RT}$ ($\tau_0 \approx 10^{-13}$ sec., Q chaleur d'adsorption). Les molécules d'eau adsorbées en couches monomoléculaires ont des valeurs de τ entre 10^{-2} et 10^2 sec. Ces temps sont donc 10^4 à 10^6 fois plus grands que $1/\omega$ pour les fréquences utilisées. Dans le temps $1/\omega$ il n'y a donc que relativement peu de molécules dans l'état désorbé. En tenant compte des propriétés de la première section de l'isotherme, les molécules ne sont donc orientables que pendant le temps de désorption τ' et non dans le temps τ . Comme Q et τ des molécules adsorbées sur la couche monomoléculaire sont beaucoup plus petits, cette représentation permet d'expliquer l'allure des isothermes. Le comportement des pertes diélectriques est très bien donné par la « chemical rate theory » de Eyring-Kauzman.

Measurements of apparent dielectric constant (ϵ) and of dielectric loss ($\tan \delta$) were carried out at frequencies of 100 kc/sec, 1000 kc/sec, and 7030 kc/sec and in the temperature range from $+ 25^\circ \text{C}$ to $- 60^\circ \text{C}$.

When plotting ϵ or $\tan \delta$ against the amount of water sorbed per gram of adsorbent (a) in mg/g, a plot is obtained that consists of three quite distinct linear sections causing two breaks. The first linear part of the $\epsilon - (a)$ —and of the $\tan \delta - (a)$ —plot shows a very low inclination and

depends hardly on temperature and frequency. At a water content of 13-14 mg/g the first break occurs, also hardly dependent on frequency and temperature at frequencies used by us. ϵ and $\tan \delta$ after the first break increase more steeply than at 1000 kc/sec and at this frequency more than at 7030 kc/sec. The second break, however, depends very much on temperature and frequency. It varies e.g. from 24 mg/g at 100 kc/sec and 20° C to 36 mg/g at — 30° C. At 1000 kc/sec, the second break is shifted from 39 mg/g (20° C) to 43 mg/g (— 20° C), and there is no break at — 30° C or temperatures below this, whereas at 100 kc/sec the second break disappears at — 40° C. Between — 40° C and — 60° C, the inclination of ϵ — (a)—and $\tan \delta$ — (a)—curves above 48 mg/g is almost zero. In this range no reversibility of ϵ and $\tan \delta$ after lowering temperature to — 60° C is to be found (hysteresis curves are obtained) [1]. (Only a part of our results is described here.)

In order to attempt an interpretation of the results mentioned above, the dynamical consideration of adsorption which is mainly developed by de Boer [2] and Frenkel [3] will be used. According to these authors, the molecules at the equilibrium of adsorption stay on the surface during the time τ (time of adsorption). For τ the equation

$$\tau = \tau_0 e^{Q/RT} \quad (1)$$

is valid. (τ_0 is the time of oscillation of the molecules in the adsorbed state and amounts nearly to 10^{-13} sec, Q is the heat of adsorption, R and T have the usual meaning.) Q being known, we are able to determine τ . For molecules sorbed in a monomolecular layer, Q amounts from 14 to 20 kcal/mole. This corresponds to τ -values from 10^{-2} to 10^2 sec. Therefore τ is at least 10^4 — 10^6 times longer than $1/\omega$ at the frequencies used. This is of great importance because of the following relation:

$$n = \sigma/\tau \quad (2)$$

(n is the number of molecules striking each cm^2 per sec or evaporating per cm^2 and sec, σ is the number of molecules sorbed per unit of surface.) From these considerations results that in consequence of the long adsorption time only a few molecules are in the desorbed state during $1/\omega$. Remembering the behaviour of the first linear section, we conclude that there is no possibility of orientation in the alternating field for molecules in the monolayer during the time τ . These molecules are able to orientate during the

desorption time τ' only. The longer $1/\omega$, the greater the number of molecules in this time which contribute to the total polarisation. It is to be noted that molecules sorbed in higher layers, are allowed to orientate to some degree, but not as much as during τ' or—in general—during a change of place. The Q-values of molecules sorbed on top of the monolayer are smaller than for the latter and amount to 14-9,7 kcal/mole (heat of condensation), as the lowest limit. Therefore τ is shorter than in the monolayer, and for this reason many dipoles are in the orientable state during $1/\omega$. This is the explanation for the sudden change in ϵ and $\tan \delta$ after completing the monolayer and also for the remarkable dependence on temperature and frequency of the curves after the first break. This is a simple model indeed, but very useful for the sake of explanation of the dielectric behaviour of sorbed molecules ¹.

A more detailed paper will be published elsewhere.

1. EBERT, G., *Kolloid-Z.*, *161*, 129, 1958.
2. DE BOER, J. H., *The dynamical character of adsorption*. Oxford, 1953.
3. FRENKEL, J., *Z. Phys.*, *26*, 117, 1924.

¹ It is to be noted that Eyring's chemical rate theory of dielectric relaxation allows a general treatment of the dielectric behaviour of sorbed water molecules.
