Dielectric Relaxation in Water Adsorbed on Alums

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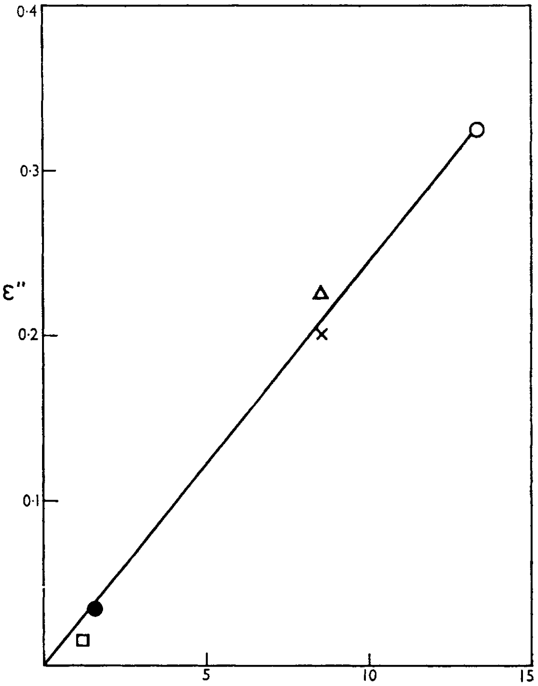
IN the course of a dielectric investigation into the dehydration and rehydration of various sulphate alums, it was found that, at a frequency of 4·0 Mc./sec., the dielectric properties were markedly sensitive to surface-adsorbed water as distinct from internal water of crystallisation. Furthermore, during rehydration the dielectric loss was found to be linearly related to the equilibrium vapour pressure of the alum. In the following it is shown that this linear relationship reflects the mechanism by which adsorbed water is attached to the surface.

Partial dehydration of 3·3—4·5 g. samples was carried out *in vacuo* at 19—22°c using the same apparatus and *Q*-meter as for a previous investigation,[1] with the exception that only one of the cylindrical condenser cells containing the sample was employed. The samples were either crushed to a fine powder (NH_4Fe and KCr alums), or used in the form of crystals of diameter up to about 1 mm. (NH_4Al, KAl, and KCr alums). Of the 12 moles of water of crystallisation originally held by each alum, 9·6, 5·8, and 1·2 moles were removed from NH_4Fe, KCr, and KAl alums respectively; the extent of dehydration of NH_4Al alum was not measured. Rehydration was carried out by the volumetric method of sharing doses of water vapour with the adsorption cell at 21·5—23°c, allowing equilibration times ranging from about 5 min. to 10 hr.

With each successive dose, the value of the dielectric loss factor, ϵ'' for a given alum and at a given pressure of water vapour in contact with the solid, was always approximately the same. Thus, as the pressure decreased during the equilibration of any one dose, ϵ'' also decreased, in spite of the fact that water was being taken up by the solid. These observations showed that it was only the adsorbed water, in equilibrium with the water vapour, that made any significant contribution to the dielectric loss at this frequency (4·0 Mc./sec.).

In the Figure, the values of ϵ'' at a constant rehydration pressure of 7 mm. are plotted against the equilibrium vapour-pressure data of Hepburn and Phillips.[2] Since the magnitude of ϵ'' is determined largely by the relaxation time, τ, *i.e.*,



FIGURE

Relationship between the dielectric loss at 4·0 *Mc./sec., in water adsorbed at a rehydration pressure of* 7 *mm., and the equilibrium vapour pressure of the alum. The vapour pressures, taken from the data* (*ref.* 2) *of Hepburn and Phillips, correspond to temperatures* (21·5—23°) *at which the experiments were carried out.*

○ NH_4Fe (crushed); × KCr;
△ KCr (crushed); ● KAl; □ NH_4Al

by the mobility of the dipoles or charge carriers in the adsorbate, it is evident from the Figure that the strength of binding of adsorbed water to the surface is closely related to the strength with which internal water of crystallisation is held inside the lattice. (The data of Hepburn and Phillips provide a measure of this latter strength.) The adsorbed water molecules probably cluster around surface cations in a comparable manner to that which occurs, more extensively, with water of crystallisation inside the lattice. The mechanism of the binding of water of crystallisation in the alums has been discussed by Hepburn and Phillips.[2]

Further interpretation of the results summarised in the Figure can be made in terms of the Debye equation for dielectric loss,

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)\omega\tau/(1 + \omega^2\tau^2) \qquad (1)$$

where ϵ_∞ is the dielectric constant at very high frequencies, ϵ° is the static dielectric constant, and ω is the angular frequency ($= 2\pi f$, where f is the frequency in c./sec.). This equation applies to both Debye and Maxwell–Wagner type mechanisms. With the present work, the only variable in equation (1) is τ, since both ϵ_0 and ϵ_∞ can be regarded as constants and ω is fixed at $8\pi \times 10^6$. Therefore, provided τ is of the order of 10^{-6} sec. or greater, the term $\omega^2\tau^2$ will be much greater than unity, in which case ϵ'' should be inversely proportional to τ. Since τ is inversely related to the mobility of the dipoles or charge carriers, it then follows that ϵ'' will be directly related to mobility.

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[1] P. G. Hall, L. Glasser, and D. D. Liebenberg, *Surface Sci.*, in the press.

[2] J. R. I. Hepburn and R. F. Phillips, *J. Chem. Soc.*, 1952, 2569.