Water Immobilized on Porous Jarosite: Dielectric and Thermal Analyses

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Water molecules in 1.6 layers on porous jarosite were anomalously immobilized in slit-like micropores of 1.0 nm width.

The thin layer of water absorbed on solid surfaces and on biopolymers has been investigated by various techniques.[1—7] The state of water on non-porous oxides depended strongly on surface coverage and monolayers could be distinguished from multilayers.[1—4] N.m.r. and dielectric properties of water adsorbed on porous substances changed in a more complex way;[5—7] the chemical and geometrical features of the surface may influence the structure of water in the vicinity of walls of the pores. The relaxation time (τ) of water adsorbed on porous as well as non-porous substances in general decreased monotonically with increasing surface coverage and approached that of ice at room temperature. In this communication, we report on the novel behaviour of water in 1.6 layers adsorbed on porous jarosite, *i.e.*, an example of the 'micropore effect' on the state of adsorbed molecules.

Porous jarosite [$KFe_3(SO_4)_2(OH)_6$] was prepared by refluxing an aqueous mixture (pH 2.0) of $Fe_2(SO_4)_3$ (0.3 M), KOH, and K_2SO_4 (saturated) for 2.5 h.[8] The precipitated material was washed well with water and characterized by *X*-ray diffraction, scanning and transmission electron microscopy (SEM and TEM), and chemical analysis.[8] After a sample had been treated at 10^{-5} Torr and 110 °C for 15 h, the adsorption isotherms for water and N_2 on porous jarosite were obtained by a gravimetric method at 18—30 and −196 °C, respectively. The dielectric properties of the adsorbed water were measured at 20 Hz—100 kHz and 30 °C, with an a.c.-bridge circuit and concentric cylindrical electrodes.[3] The heat of wetting for jarosite adsorbing various amounts of water was measured by a microcalorimeter at 30 °C.

The dielectric constant (ε) increased with surface coverage (θ) [the ratio of water adsorbed to the amount adsorbed at saturation (53.5 mg/g)], and water in bilayers adsorbed on porous jarosite was distinguished clearly from that in monolayers ($\theta < 1$) and in multilayers ($\theta > 2$). Figure 1 shows the relationship between the dielectric relaxation time (τ), obtained from a Cole–Cole plot, and θ. The τ value remained constant (6×10^{-5} s) for less than monolayer coverage, but increased steeply across $\theta = 1$ and reached a maximum value of 6×10^{-4} s at *ca.* $\theta = 1.6$, subsequently decreasing to 10^{-6} s. The maximum τ value was 300 times larger than that of ice at room temperature, 2×10^{-6} s.[9] If the τ *vs.* temperature curve for ice[9] is extrapolated to low temperature, a τ value of 6×10^{-4} s relates to −32 °C. The water in the 1.6 coverage layers adsorbed on 'porous' jarosite was stabilized by $RT \approx 0.3$ kJ mol^{-1} to make a 'cold' ice. Thus, when water was adsorbed bimolecularly on porous jarosite, water molecules were immobilized at room temperature.

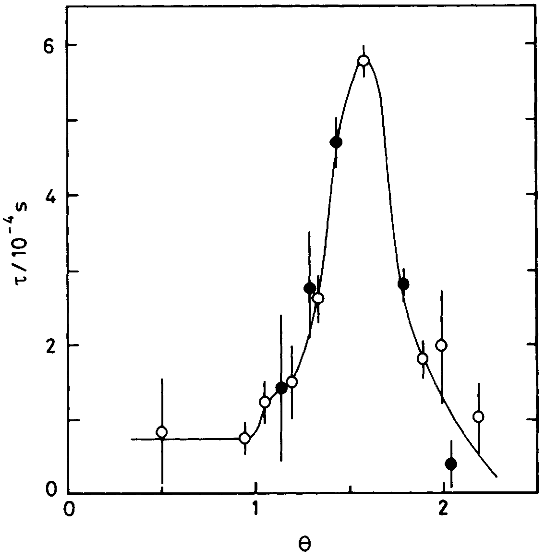

Figure 1. Variation of dielectric relaxation time (τ) with surface coverage of water adsorbed on porous jarosite (θ). ○ adsorption; ● desorption.

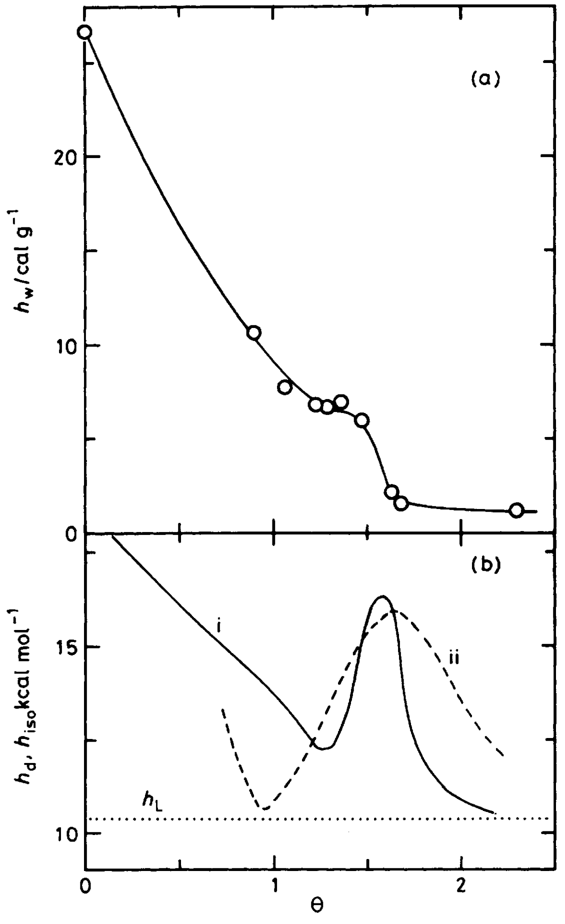

Figure 2. (a) The relationship between heat of wetting for porous jarosite pre-adsorbing water and surface coverage (θ). (b) Variation of differential adsorption heat (h_d, i) and isosteric heat (h_{iso}, ii) with surface coverage (θ); h_L is the heat of liquefaction per mol of water vapour.

The heat of wetting h_w of porous jarosite pre-adsorbing water decreased abruptly across $\theta = 1.6$ [Figure 2(a)] to less than the value of the heat of liquifaction per mol of water vapour ($h_L = 10.4$ kcal mol^{-1}; cal = 4.184 J), indicating that the jarosite crystals have a narrow pore size distribution and that the pores are filled with water around $\theta = 1.6$.[10] N_2 adsorption at −196 °C suggested the existence of micropores of 1.0 nm mean width (in terms of the *t* plot).[8] SEM and TEM images showed that porous jarosite has a piled structure of thin layered crystals. We propose that porous jarosite has slit-like micropores with a width of 1.0 nm, whose walls are parallel to the hexagonal layers of jarosite and occupy over 90% of the total surface area.[8] Most water adsorbed on porous jarosite must therefore exist in the slit-like micropores. Since the diameter of a water molecule is approximately 0.3 nm, the 1.0 nm micropores are filled with 3 layers of adsorbed water, *i.e.*, $\theta = 1.5$.

The relaxation mechanism in pure ice is believed to be a reorientation of a pair of D- and L-orientational defects.[11] The relaxation time of water in the monolayer on porous jarosite was smaller than those on hematite and silica gel.[1,6] Hexagonal, skeletal OH rings exist on the surface of jarosite, and water molecules could form a tridentate hydrogen bond with the three OH groups there. The hydrogen-bonded water may then rotate freely to form D- and L-orientational defects. In the case of porous jarosite, therefore, it is supposed that at $\theta \approx 1.6$ the orientation process may be disturbed by the second layer bridging the first layers adsorbed on both walls of the micropores. The bridging effect may occur through hydrogen bonds, suggested by the differential adsorption h_d and isosteric heats h_{iso} [Figure 2(b)]. The h_d value was calculated from the h_w *vs.* θ curve and that of h_{iso} by application of the Clapeyron–Clausius equation to water adsorption isotherms at different temperatures (18—30 °C). These heats revealed a maximum around $\theta = 1.6$ and the difference between the maximum value and h_L, 6 kcal/mol^{-1}, approximated the hydrogen bonding energy.

The micropore effect such as observed in porous jarosite was recently reported for NO adsorption on activated carbon fibre.[12] Though NO has a critical point of −93 °C, NO was adsorbed by the micropore-filling mechanism in slit-like micropores 0.8 nm in width at room temperature and was converted into a dimer $(NO)_2$ in the micropores. It is considered that such micropore effects may result not only from the shape and size of the micropores, but also from the geometrical array of adsorption sites on walls of micropores, since no similar effects were observed in other porous adsorbents investigated.

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