undoubtedly similar. The relative inability of adsorbed CO to undergo electrooxidation on ordered Rh(111) in the presence of other species, including solution CO, may be related to the strongly chemisorbing properties of this surface. Thus, the electrooxidation of adsorbed CO and other chemisorbed organic fragments is considered to involve reaction with coadsorbed oxygen, possibly at the edges of oxygen "islands".<sup>27</sup> The nucleation and growth of such structures appears to have an important influence on the kinetics of CO electrooxidation on single-crystal<sup>27</sup> as well as polycrystalline platinum.<sup>28</sup> We can surmise, then, that the formation of such "catalytic oxygen domains" on Rh(111) is hampered severely by readsorption of other species, even CO.

While surface disordering of Rh(111) does engender a degree of electrocatalytic activity, this is still markedly below that observed

(27) For a recent discussion, see: Love, B.; Lipkowski, J. ACS Symp. Ser. 1988, No. 378, 484.

(28) For example, Conway, B. E. In Electrodes of Conductive Metal Oxides, Part B; Trassati, Ed.; Elsevier: New York, 1981; p 433.

for platinum.<sup>5</sup> This property extends to polycrystalline rhodium.<sup>24</sup> As suggested by earlier results for formic acid electrooxidation on polycrystalline surfaces,<sup>14</sup> the lower electrocatalytic activity for rhodium is consistent with an anticipated greater stability of chemisorbed intermediates. If this general notion is correct, then rhodium could provide a revealing substrate for infrared spectroscopic detection of reaction intermediates (cf. ref 29).

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Registry No. Rh, 7440-16-6; Pt, 7440-06-4; CO, 630-08-0; CO<sub>2</sub>, 124-38-9; formic acid, 64-18-6; methanol, 67-56-1; ethanol, 64-17-5; acetaldehyde, 75-07-0; ethylene glycol, 107-21-1; glyoxal, 107-22-2; oxalic acid, 144-62-7; acetic acid, 64-19-7.

(29) Nichols, R. J.; Bewick, A. Electrochim. Acta 1988, 33, 1691.

# Nuclear Magnetic Resonance and Dielectric Relaxation Studies of Water Adsorbed on Synthetic Porous Alunite

# Sumio Ozeki,\*

Department of Chemistry, Faculty of Science, Chiba University, Yayoi-cho 1-33, Chiba 260, Japan

# Yuichi Masuda, and Hirotoshi Sano

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, 2-1-1 Fukazawa, Setagaya 158, Tokyo, Japan (Received: March 31, 1989)

Adsorbed water on a synthetic, porous alunite, having slitlike micropores of 1.1-nm width, was studied by <sup>1</sup>H NMR and dielectric relaxation measurements from -80 to +30 and 20 to 40 °C, respectively. Adsorbed water was distinguished by the dielectric permittivity and loss for mono-, bi-, and trimolecular layers. The motional mode observed by  $T_1$  depends on the surface coverage  $\theta$ : (i) Water molecules in a monolayer seem to have a mode of rotational motion and show no phase transition with decreasing temperature down to -80 °C. (ii) Those in a multilayer, having a mode of translational motion, freeze at about -30 °C. (iii) Water molecules in a 1.3 layer ( $\theta = 1.3$ ) change their motional mode from rotation to translation across about -30 °C. The variation of the line width of NMR spectra suggests that water mobility in the monolayer increases with an increase in the monolayer density. The dielectric relaxation time of adsorbed water is a maximum value of  $1.2 \times$  $10^{-3}$  s at  $\theta = 1.3$ . The extreme immobilization of water molecules in a 1.3 layer was attributed to a filling of the slitlike micropores with water molecules, which occurred due to water molecules in the second layer bridging the first layers-adsorbed on both walls of the micropores--through hydrogen bonding. The dielectric relaxation mechanism seems to change from the orientational polarization to the interfacial polarization across  $\theta = 1.3$ .

# Introduction

Adsorbed water on solid surfaces is immobilized like ice.<sup>1-12</sup> The behavior of water surrounded by potential walls, as in pores,

- (1) McIntosh, R. L. Dielectric Behavior of Physically Adsorbed Gases; Dekker: New York, 1966; Chapter 5.
- (2) MaCafferty, E.; Pravdic, V. H.; Zettlemoyer, A. C. Trans Faraday Soc. 1970, 66, 1720. MaCafferty, E.; Zettlemoyer, A. C. J. Colloid Interface
- Sci. 1970, 34, 452; Discuss. Faraday Soc. 1971, 52, 239.
   (3) Dransfeld, K. J. Chem. Phys. 1962, 36, 1574. Baldwin, M. G.; Mor-
- (4) (a) Morimoto, T.; Iwaki, T. J. Chem. Soc., Faraday Trans. 1 1987, 83, 943. (b) Iwaki, T.; Morimoto, T. Ibid. 1987, 83, 957. (c) Iwaki, T.; Morimoto, T. Langmuir 1987, 3, 282.
  (5) Konche K. Scher, S. Scher, Scher, S. Scher, Scher, Scher, Scher, row, J. C. Ibid. 1962, 36, 1591
- (5) Kaneko, K.; Serizawa, M.; Ishikawa, T.; Inouye, K. Bull. Chem. Soc.
- Jpn. 1975, 48, 1764.
- (6) Zimmerman, J. R.; Lasater, J. A. J. Phys. Chem. 1958, 62, 1157.
   (7) Hall, P. G.; Williams, R. T.; Slade, R. C. T. J. Chem. Soc., Faraday Trans. 1 1985, 81, 847. (8) Brey, W. S., Jr.; Lawson, K. D. J. Phys. Chem. 1964, 68, 1474.
- (9) Resing, H. A.; Thomson, J. K.; Krebs, J. J. J. Phys. Chem. 1964, 68, 1621. Foster, K. R.; Resing, H. A. Ibid. 1976, 80, 1390.
- (10) Lipsicas, M.; Straley, C.; Costanzo, P. M.; Giese, R. F., Jr.; J. Colloid
- (11) Lipstan, IA, Bitter, Y. J. Colloid Interface Sci. 1974, 46, 232.
  (11) Pearson, R. T.; Derbyshire, W. J. Colloid Interface Sci. 1974, 46, 232.
  (12) Clark, J. W.; Hall, P. G.; Pidduck, A. J.; Wright, G. J. J. Chem. Soc., Faraday Trans. 1 1985, 81, 2067.

may be peculiar, and recently, such a pore effect was found in the dielectric relaxation time of water on the porous jarosite.<sup>13</sup> The dielectric relaxation time of water on it changed with surface coverage, passing through a maximum value of  $6 \times 10^{-4}$  s for 1.6 layers. The maximum relaxation time corresponds to that of ice at -32 °C. This immobilization of water molecules in 1.6 layers was attributed to a filling of the slitlike micropores with water molecules. However, the relaxation mechanism could not be deduced from the results, although the orientational relaxation was assumed.

Alunite  $(KAl_3SO_4(OH)_6)$  has the same crystal structure<sup>14</sup> as jarosite (Figure 1). Porous alunite with a large specific surface area<sup>15</sup> may be expected to have slitlike micropores, as in the porous jarosite. We can obtain the dynamical information of adsorbed water in pores of alunite by <sup>1</sup>H NMR, unlike the case of porous jarosite that contains paramagnetic Fe(III) ions. The chemical and geometrical features of the surface may influence the structure

<sup>(13)</sup> Ozeki, S. J. Chem. Soc., Chem. Commun. 1988, 1039; Langmuir

<sup>1989, 5, 181.</sup> (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, R.; Bradley, (14) Hendricks, S. B. Am. Mineral. 1937, 22, 773. Wang, S. Wa

<sup>(15)</sup> Kurata, M.; Kaneko, K.; Inouye, K. J. Phys. Chem. 1984, 88, 2119.



 $\bigcirc$ :OH,  $\bigcirc$ :O, O:AL,  $\circ$ :S,  $\bigcirc$ :K



Figure 1. Schematic structure of alunite.

and dynamic properties of water in the vicinity of the walls of the pores. Therefore, NMR signals of adsorbed water will give some information on the pores and surfaces as well as the dynamic properties of water, although NMR of water adsorbed on porous substances changes in a complex way.<sup>6,9-11</sup>

In this paper, water adsorbed in slitlike micropores of a synthetic porous alunite is examined by means of <sup>1</sup>H NMR as well as dielectric relaxation, and the pore effect on their dynamic properties is discussed.

# **Experimental Section**

Alunite was prepared by refluxing a mixed solution (pH 3.5) of 0.3 mol/dm<sup>3</sup> Al<sub>2</sub> (SO<sub>4</sub>)<sub>3</sub>, KOH, and K<sub>2</sub>SO<sub>4</sub> (saturation at 100 °C) at the boiling point for 2.5 h, according to the preparation method for a porous jarosite.<sup>15,16</sup> The precipitates were washed with distilled water and characterized by an X-ray diffraction (XRD) method and transmission (TEM) and scanning (SEM) electron microscopic observations. N<sub>2</sub> adsorption on alunite, dired at 110 °C and 10<sup>-5</sup> Torr for 15 h, was measured by a gravimetric method<sup>13</sup> at -196 °C.

Adsorption isotherms for water on alunite were obtained by a procedure similar to the N<sub>2</sub> adsorption at  $(18-40) \pm 0.02$  °C. Dielectric properties of water adsorbed on alunite at (20-40)

 $\pm$  0.1 °C were measured with an ac bridge circuit and a concentric,



Figure 2. Adsorption isotherm of  $N_2$  on a porous alunite at -196 °C.

cylindrical, aluminum cell at 0.02–100 kHz and each temperature, as previously reported.<sup>13</sup>

<sup>1</sup>H NMR was measured by a JEOL Model FX-200 Fourier transform spectrometer under the magnetic field, 4.7 T (200 MHz for the proton resonance). The spin-lattice relaxation time,  $T_1$ , of the <sup>1</sup>H nucleus of water was determined by the saturationrecovery method with the pulse sequence of [-(HS)-90° pulse-(HS)-t-90° pulse-T-], (HS, homo spoiling pulse; t, pulse interval; t, waiting time). A typical 90° pulse was  $15.0 \pm 0.1 \ \mu s$ . The  $T_1$  value for each sample was determined by a series of measurements with different time intervals of more than 18 and with a waiting time of more than  $20T_1$ . The temperature of the samples, -80 to +30 °C, was controlled within 0.5 °C by heating dry air, performed with a variable-temperature control unit (JEOL PVTS2 type). The 200-mg samples were placed into a 5-mmdiameter NMR cell, which was dried by the procedure similar to the  $N_2$  adsorption and then was sealed off after the sample had adsorbed definite amounts of water at various relative pressures and 30 °C.

#### Results

Figure 2 shows the adsorption isotherm for N<sub>2</sub> on the prepared alunite. The specific surface area of the alunite  $(a_s)$ , which is calculated by the BET equation, was 265 m<sup>2</sup>/g. Such a large  $a_s$ value results from the inner surfaces of pores in the alunite crystals, since the outer surface area of layered crystals (average size, ~1  $\mu$ m<sup>2</sup>) is estimated to be about 200 m<sup>2</sup>/g, even if the thickness of the crystals is 3.4 nm, corresponding to that of two repeating layers. The alunite crystal has a lamellar structure composed of Al(O, OH) and (K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>) layers (Figure 1). Therefore, such pores are expected to be slitlike, considering that the pores appeared during washing by release of K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, and other included materials.<sup>13,15,16</sup>

The t plot<sup>17,18</sup> of N<sub>2</sub> adsorption for the porous alunite is composed of two linear sections whose crossing point indicates the existence of micropores of 1.1-nm width (Figure 3). The specific surface area,  $a_s' = 271 \text{ m}^2/\text{g}$ , obtained from the steep slope of the straight line passing through the origin, agrees approximately with the  $a_s$  value. This suggests that most of the surface area of the porous alunite may arise from the walls (the inner surface) of the micropores. The outer surface area,  $a_o'$ , was estimated from

<sup>(16)</sup> Ozeki, S.; Inouye, K. J. Colloid Interface Sci. 1988, 125, 356.

<sup>(17)</sup> Lippens, B. C.; De Boer, J. H. J. Catal. 1965, 4, 319.

<sup>(18)</sup> Gregg, S. J.; Sing, K. S. W. Adsorption Area and Porosity; Academic Press: New York, 1982. The thickness of  $N_2$  film adsorbed on the solid surface were the values used in this text.

TABLE I: Characteristic Values of a Porous Alunite from Gas Adsorption

	BET plot		t plot				
adsorbent	$v_{\rm m}$ , mmol/g	$a_{\rm s}$ , a m <sup>2</sup> /g	$v_{\rm m}'$ , mmol/g	$a_{\rm s},{\rm m}^2/{\rm g}$	$a_0^{i}, m^2/g$	$v_t$ , mL/g	<i>l</i> , <sup><i>b</i></sup> nm
N <sub>2</sub>	2.72	265	2.78	271	15	0.166	1.1
H₂O	4.49	287	4.59	293			

<sup>a</sup> Molecular area: 0.162 nm<sup>2</sup> for N<sub>2</sub>; 0.106 nm<sup>2</sup> for H<sub>2</sub>O. <sup>b</sup> Width of slitlike micropores.



Figure 3. t plots for  $N_2$  (solid line) and  $H_2O$  (broken line) on a porous alunite. The reference curves for the thickness t of  $N_2$  and  $H_2O$  films were referred to ref 18 and the adsorption isotherm for water on a non-porous iron oxyhydroxide ( $\gamma$ -FeOOH), respectively.

the gentle slope of the higher t region to be less than  $15 \text{ m}^2/\text{g}$ . Various characteristic values for the porous alunite are summarized in Table I.

The pore size distribution curve was calculated from the desorption branch of the isotherm by means of the Innes method<sup>19</sup> for slitlike pores. Two maxima exist at 1.0- and 1.5-nm widths in the curve. The pore volume decreases gradually from the maximum porosity at 1.5 nm to a zero value at 4 nm. This broad distribution of pores seems to correspond to the subtle stepwise change in the region of  $p/p_0 \approx 0.25$  on the adsorption branch of the N<sub>2</sub> adsorption isotherm. The amount of H<sub>2</sub>O adsorbed on the alunite (Figure 4) reveals a steep rise from moderate pressure and is mcuh more than that of adsorbed N<sub>2</sub>. These suggest that the adsorption, especially of polar H<sub>2</sub>O molecules, can occur in the intersticies between thin crystals, because the lamella of alunite cannot swell.

The adsorption isotherms of  $H_2O$  on the porous alunite have large hysteresis loops (Figure 4), unlike the  $N_2$  adsorption isotherm. The monomolecular amounts for water,  $v_m$  and  $v_m'$ , were calculated from the BET plot and the t plot (Figure 3), respectively. The t plot for  $H_2O$  suggests that the alunite is mesoporous. These values are also listed in Table I.

The application of the Clapeyron-Clausius equation to the adsorption isotherms at different temperatures (18-30 °C) yields the isosteric heat of H<sub>2</sub>O adsorption,  $q_{\rm st}$ .<sup>20</sup> The  $q_{\rm st}$  value decreases



Figure 4. Adsorption isotherms of H<sub>2</sub>O on a porous alunite at 20 ( $\Delta$ ,  $\Delta$ ), 30 (O,  $\odot$ ), and 40 °C ( $\Box$ ,  $\blacksquare$ ): open, adsorption; filled, desorption.



Figure 5. Isosteric heat  $(q_{si})$  for  $\theta$  of H<sub>2</sub>O adsorbed on porous alunite. The  $h_L$  value indicates the heat of liquefaction per mol of water vapor (10.41 kcal/mol).

with  $\theta$  to the  $h_L$  value, through a maximum (15.2 kcal/mol) at  $\theta \approx 1.3$ , as shown in Figure 5. Here,  $\theta$  is the surface coverage that is defined by the ratio of the adsorbed amount to  $v_m$ , and  $h_L$  is the heat of liquefaction per mole of water vapor, 10.41 kcal/mol. The monotonous decrease of  $q_{st}$  in the monolayer coverage region

<sup>(19)</sup> Inness, W. B. Anal. Chem. 1957, 29, 1069. Daimon, M.; Kondo, R. Nippon Kagaku Kaishi 1972, 238.

<sup>(20)</sup> Zettlemoyer, A. C.; Micale, F. J.; Klier, K. In Water; Franks, F., Ed.; Plenum Press: New York, 1975; Vol. 5, p 249.



Figure 6. Integral intensity (A), half-height width  $\nu_{1/2}$  (B), and spinlattice relaxation rate  $T_1^{-1}$  (C) of <sup>1</sup>H NMR signals of H<sub>2</sub>O adsorbed on a porous alunite as a function of temperature. Surface coverage ( $\theta$ ): **O**, 0.35; **O**, 0.6; **O**, 0.75; **O**, 1.05; **O**, 1.35; **O**, 1.85.

indicates heterogeneity of the alunite surface. The appearance of the maximum seems to be peculiar in the alunite system. The difference (5 kcal/mol) between the maximum value and the  $h_L$  value is comparable to the formation energy of one hydrogen bond per water molecule.

The line shape of all <sup>1</sup>H NMR spectra was regarded as a single Lorentzian. Figure 6 shows the variations of the integrated intensity (A), the half-height width of the peak (B), and the spin-

lattice relaxation rate (C),  $T_1^{-1}$ , of the proton signals of water adsorbed on the alunite with temperature. The changes of these values are very complex, in comparison with other water-adsorbent systems.<sup>7-11</sup>

The dependence of the peak intensity on temperature changes clearly across  $\theta \approx 1.3$ . For  $\theta > 1.3$ , the number of detectable (mobile) protons decreases steeply below -30 °C. This suggests that water molecules in multilayers freeze. On the other hand, the motion of water molecules for  $\theta < 1$  would be restricted even at room temperature, as suggested by the extremely small peak intensities in comparison with those for the bilayer. This motional restriction may prevent water molecules in the monolayer from so-called freezing to lead to the small temperature dependence of the peak intensity.

The  $\nu_{1/2}$  values for  $\theta < 1$  are very large in comparison with other water-solid systems and increases continuously with a decrease in temperature, whereas  $\nu_{1/2}$  for  $\theta > 1.3$  increases steeply below about -30 °C. This also suggests that water in a monolayer on the alunite does not freeze and is strongly immobilized on the surfaces. Water for  $\theta > 1.3$  freezes below -30 °C to become "ice", which could be different from bulk ice in the degrees of freedom. In addition, the large  $\nu_{1/2}$  values, in comparison with those for mesoporous silica gels,<sup>7,11</sup> arise from the micropore effects, as discussed later.

 $T_1^{-1}$  decreases at  $\theta = 0.75$  and increases at  $\theta = 1.35$  and 1.9 as temperature increases. At  $\theta = 1.1$ , both tendencies of the temperature dependence of  $T_1^{-1}$  appear across about -25 °C. Such a change in the temperature dependence across  $\theta \approx 1.3$  would be ascribed to different motions of adsorbed water.

The integrated intensity,  $\nu_{1/2}$ , and  $T_1^{-1}$  are replotted against  $\theta$  in Figure 7. The integrated intensity increases abruptly at  $\theta = 1$  and reaches a maximum value near  $\theta = 1.3$ , irrespective of temperature.  $\nu_{1/2}$  decreases with an increase in  $\theta$  and approaches a constant value at  $\theta > 1.3$ . This indicates that water molecules in a first layer become more mobile with the increasing water density of the layer and, on the one hand, that the mobilities of water molecules in a bilayer and probably a multilayer remain almost unchanged. On the other hand,  $T_1^{-1}$  for  $\theta < 1.3$  decreases with increasing  $\theta$ , which seems to be contradictory with the behavior of  $\nu_{1/2}$  with  $\theta$  and to be out of the general concept. Therefore, we again suppose that water adsorbed on the alunite would change the dynamic properties in the region  $\theta = 1.3$ .

The dielectric permittivity  $(\epsilon')$  increased monotonously with  $p/p_0$  and steeply at  $p/p_0 > 0.4$ . The  $\epsilon'$  value at a relative pressure increased with increasing temperature. The dielectric isotherms revealed a large hysteresis at low frequency while the hysteresis loop shifted to higher pressure with an increase in frequency. These tendencies were independent of temperature. Water in the first layer contributed little to the dielectric constant as in metal oxides<sup>2,6</sup> and porous jarosite.<sup>13</sup> The dielectric permittivity increases linearly with  $\theta$  in three regions,  $\theta < 1$ ,  $1 < \theta < 2$ , and  $\theta > 2$ , regardless of temperature (Figure 8). This suggests that the lateral interaction between adsorbed water molecules is independent of  $\theta$  in each layer. Water in ca. 1.5-2 layers seems to interact specifically between adsorbed water molecules or have two modes whose portion changes, as inferred by the deviation from the linearity of the  $\epsilon' - \theta$  curve. The dielectric loss ( $\epsilon''$ ) also increased with  $\theta$  and gave three regions with different slopes, as in the water-jarosite systems.13

The dielectric relaxation time,  $\tau_d$ , of water adsorbed on the porous alunite (Figure 9) was calculated by the Cole–Cole plot.<sup>21</sup> A distribution of  $\tau_d$  values was suggested by the deviation from a semicircle of the Cole–Cole plot. The  $\tau_d$  values near  $\theta = 2$  are comparable with that of ice at corresponding temperatures, e.g.,  $2 \times 10^{-6}$  s at 30 °C.<sup>22</sup> The maximum  $\tau_d$  value at  $\theta = 1.2$ , e.g.,  $1.2 \times 10^{-3}$  s at 30 °C, is approximately 600 times larger than that of ice at room temperature. This reveals the immobilization of water molecules in 1.2 layers, irrespective of temperature (20–40 °C).

<sup>(21)</sup> Cole, K. S.; Cole, R. H. J. Chem. Phys. 1941, 9, 341.

<sup>(22)</sup> Auty, R. P.; Cole, R. H. J. Chem. Phys. 1952, 20, 1309.





**Figure 7.** Integral intensity (A), half-height width  $\nu_{1/2}$  (B), and spinlattice relaxation rate  $T_1^{-1}$  (C) of <sup>1</sup>H NMR signals as a function of surface coverage of H<sub>2</sub>O adsorbed on a porous alunite. Temperature (°C):  $\bullet$ , -80;  $\bullet$ , -60;  $\bullet$ , -30;  $\bullet$ , 0;  $\circ$ , 30.

The activation energy, E, of the dielectric relaxation is estimated from the change of relaxation time at a given  $\theta$  value with temperature by

$$\tau_{\rm d}^{-1} = e^{-E/RT} \tag{1}$$

where R is the gas constant and T is the absolute temperature.

**Figure 8.** Variations of dielectric permittivity with coverage  $\theta$  of H<sub>2</sub>O adsorbed on a porous alunite at 20 (A), 30 (B), and 40 °C (C). Frequency (kHz):  $\Phi$ , 0.02;  $\Phi$ , 0.1;  $\Phi$ , 1; O, 10;  $\Phi$ , 100.

The activation energy seems to decrease steeply with  $\theta$  from 0.35 eV for  $\theta = 0.85$  to ca. 0.22 eV for  $\theta > 1$ , besides from large ambiguity of *E* values.

# Discussion

Water Adsorption in 1.1-nm Slitlike Micropores. The porous alunite has the maximum porosity around 1.1 nm in width. The micropores will be slitlike,<sup>13,15</sup> as expected from the layered structure of alunite crystal. Most water molecules adsorbed may



Figure 9. Variations of dielectric relaxation time  $\tau_d$  with coverage  $\theta$  of H<sub>2</sub>O adsorbed on a porous alunite. Temperature (°C):  $\bullet$ , 20;  $\bullet$ , 30;  $\bullet$ , 40.

exist in the micropores, because the inner walls comprise ca. 95% of the surface area. A maximum of water layers in the slitlike micropores, i.e., three layers, can be formed when  $\theta = 1.5$ , assuming 0.30 nm for the diameter of a water molecule. In practice, many dynamic properties (Figures 6, 7, and 9) indicate the existence of the micropores that are filled with three layers ( $\theta \approx 1.3$ ). The isosteric heat also supported this idea, as the maximum on the  $q_{st}$ - $\theta$  curve suggests (Figure 5). The  $q_{st}$  maximum means that the alunite has a relatively narrow micropore size distribution and that water molecules in the second layer would bridge the first layers, adsorbed on both walls of the micropores, through hydrogen bonding.

At  $\theta > 1.3$ , water adsorbs only on the outer surface of the porous alunite to form multilayers. Therefore, the true layer number for  $\theta > 1.3$  could be much more than the  $\theta$  value, because  $\theta$  is defined on the basis of the monolayer capacity that mostly arises from the inner surface. This explains why the isosteric heat for  $\theta >$ 1.3 approaches rapidly to the  $h_L$  value and why the  $\epsilon -\theta$  curves deviate upward from the straight lines and steeply increase with  $\theta$ . The porous alunite has also some mesopores. Most portions of these mesopores seem to be the intersticies between thin-layer crystals rather than mesopores in a crystal that is nonswelling, because a polar molecule, e.g.,  $H_2O$ , can penetrate into the intersticies, but a nonpolar molecules, e.g.,  $N_2$ , cannot (Figure 3).

Characteristics of Water on Porous Alunite. The difference between silica systems and the alunite system will arise mainly from that between meso- and micropores. An abrupt drop of the NMR signal intensity for multilayer at 0 °C was not observed in the alunite system, unlike silica systems (average pore size, 3.0 nm).<sup>11</sup> The  $\nu_{1/2}$  values of water on the alunite were much larger than those (<3 kHz) of silica gels.<sup>7,11,23-25</sup> These infer that little waterlike bulk water is adsorbed on the porous alunite, whose micropores are much smaller than those of silica gels, 3–10 nm. Such a signal broadening in the porous alunite systems may result from the low mobility of water molecules in the narrow slit, the dipolar effect due to the OH proton on the micropore walls, and the anisotropic effect of chemical shift.

The decreases of  $T_1^{-1}$  and  $\nu_{1/2}$  with increasing  $\theta$  (Figure 7B,C) seem to be inconsistent with each other as to the mobility of water molecules or protons (vide ante). Additionally, the temperature dependence of  $T_1^{-1}$  changed markedly across  $\theta = 1.3$ : the temperature coefficients were negative for  $\theta < 1$  and positive for  $\theta > 1.3$ . These behaviors may be interpreted by the change of the motional mode of adsorbed water, associated with the filling of

the micropores with water. The maximum of the integral intensity and  $\nu_{1/2}$  near  $\theta = 1.3$  (Figure 7A,B) also relates to the water filling.

Such a micropore effect appears as the maxima at  $\theta = 1.3$  in the  $\tau_d$ - $\theta$  and  $q_{st}$ - $\theta$  curves, as in the porous jarosite system.<sup>13</sup> This behavior seems to be peculiar, since the dielectric relaxation time of water adsorbed on porous as well as nonporous substances in general decreases monotonously with increasing surface coverage and approaches that of ice at room temperature.<sup>1-4,7,25</sup> The maximum  $\tau_d$  value near  $\theta = 1.3$  is much larger than that of ice.

<sup>1</sup>H NMR Relaxation and Motional Modes of Adsorbed Water. The NMR spectra had no fine structure (no powder pattern), and their line shapes were approximately single Lorentzian.  $T_2$  values were smaller than  $T_1$  values. We, therefore, suppose that  $v_{1/2}$  may result from the dipolar field due to the magnetic moments of neighboring protons of an adsorbed water. Then, the relaxation rate is given by <sup>26a</sup>

and

$$1/T_2 \approx \pi \nu_{1/2} \approx M_2 \tau \tag{2}$$

$$M_2 = \text{const} \times \sum r_{jk}^{-6} \tag{3}$$

where  $M_2$  is the second moment,  $\tau$  the correlation time, and  $r_{ik}$ the distance between protons j and k. From eq 2 and 3, the  $\nu_{1/2}$ value is determined by the values of  $\tau$  and  $M_2$ , i.e., a motional mode of a water molecule, the number of protons, and their array. The narrow slit of the alunite may restrict the motion of adsorbed water to lead to large  $\tau$ . This motional restriction would be especially significant at  $\theta > 1$ , because a vertical motion to the walls of the narrow slit is restricted in comparison with that in mesopores of, e.g., silica gels. Protons on pore walls would contribute to  $M_2$  even if adsorbed water molecules make a rapid rotation or translational motion, because the walls do not move against adsorbed water. The much larger  $\nu_{1/2}$  values of the alunite than those of silica gels, however, seem to arise not from  $M_2$  but from large  $\tau$  due to the micropore effect of the alunite, since the number of OH groups on the pore walls of alunite,  $6 \text{ OH/nm}^2$ estimated from the crystal structure (Figure 1), is comparable to that of silica gels,  $4.5-7.7 \text{ OH/nm}^{2.7,27}$ 

The exchange of water molecules between a first layer and a second layer on the alunite surfaces would be much more rapid than  $T_2 (\sim 10^{-3} \text{ s})$ ,<sup>7,11</sup> since the line shape is single Lorentzian. Thus, the  $\tau$  value of water molecules in the first layer at least satisfies the condition  $T_2 \gg M_2^{1/2}$ . Since  $M_2^{1/2}$  of the rigid lattice, e.g., ice, is 50–100 kHz, water molecules in the first layer may have a motion on the order of  $\tau \ll 10^{-5} \text{ s}$ .

The BPP theory<sup>26b</sup> gives

$$\frac{1}{T_1} = \frac{2}{3} M_2 \left( \frac{\tau}{1 + \omega_0^2 \tau^2} + \frac{4\tau}{1 + 4\omega_0^2 \tau^2} \right)$$
(4)

where  $\omega_0$  is the resonance frequency (= $2\pi \times 200 \text{ MHz} \approx 10^9 \text{ s}^{-1}$ ).  $T_1^{-1}$  increases with increasing temperature at  $\theta > 1.3$  (Figure 6C). This means  $\omega_0^2 \tau^2 \gg 1$ , i.e., the existence of a slow motion of  $\tau \gg 10^{-9}$  s. On the other hand, the decrease of  $T_1^{-1}$  for  $\theta < 1.3$ with increasing temperature means  $\omega_0^2 \tau^2 \ll 1$ , i.e., the existence of a certain rapid motion of  $\tau \ll 10^{-9}$  s. These reveal that the motional mode changes across  $\theta \approx 1.3$ .

Two types of motion of water molecules in the monolayer seem to be possible: one is the rotation of a water molecule at the adsorption site; the other is the lateral diffusion of a water molecule along the walls of the pores. The diffusion constant of water in multilayers on the wide-pore gels was  $(0.7-5) \times 10^{-10} \text{ m}^2/\text{s}^{28}$ , which corresponds to  $\tau \approx 10^{-10} \text{ s}$ . The motion of water molecules

(28) Morariu, V. V.; Mills, R. Z. Z. Phys. Chem. (Munich) 1972, 79, 1.

 <sup>(23)</sup> Sermon, P. A. J. Chem. Soc., Faraday Trans. 1 1980, 76, 885.
 (24) Rennie, G. K.; Clifford, J. J. Chem. Soc., Faraday Trans. 1 1977, 73, 680.

<sup>(25)</sup> Clifford, J. In Water; Franks, F., Ed.; Prenum Press: New York, 1975; Vol. 5, p 75.

<sup>(26)</sup> For example: Abragam, A. Principles of Nuclear Magnetism; Oxford University: Hong Kong, 1983; (a) p 39, (b) p 300.
(27) Kondo, S.; Saito, Y.; Ishikawa, T.; Yamauchi, H. In Adsorption at

<sup>(27)</sup> Kondo, S.; Saito, Y.; Ishikawa, T.; Yamauchi, H. In Adsorption at the Gas-Solid and Liquid-Solid Interface; Rouquerol, J., Sing, K. S. W., Eds.; Elsevier: New York, 1982; p 245. Kondo, S. Adsorpt. Sci. Technol. 1986, 3, 109. Armited, C. G.; Tyler, A. J.; Hambleton, F. H.; Mitchell, S. A.; Hockey, J. A. J. Phys. Chem. 1969, 73, 3947. Kiselev, V. F.; Krylov, O. V. Adsorption Processes on Semiconductor and Dielectric Surfaces; Gomer, R., Ed.; Springer: New York, 1985; Vol. 32, p 106.

in micropores of the alunite probably would be slower than that of water in the wide-pore gels. Therefore, it is likely that the rapid motion in the monolayer is rotation rather than translation. This seems to be consistent with the fact that water molecules in the first layer are bound strongly on surfaces, as shown by the large isosteric heat (Figure 5).

The alunite surface has hexagonal, skeletal OH rings (Figure 1). A water molecule may be trapped in the center of the ring, probably by a tridentate hydrogen bond,13 and the trapped water may rotate. This trapped water would comprise ca. 20% of the monolayer capacity. The rest of the monolayer may be more diffusible than the trapped water. The two motional modes in a monolayer might relate to the change in  $\nu_{1/2}$  and  $T_1^{-1}$  in the range  $\theta = 0.6-1$  at 30 °C (Figure 7B,C). Water molecules in a first layer become more mobile with the increase in the density of monolayer, as seen in Figure 7B. This might be attributed to the exchange between hydrogen-bonded water molecules with surface OH groups and the diffusible water molecules.

The variation of  $\nu_{1/2}$  reveals the quenching process of the lateral diffusion with a decrease in temperature. When water molecules are trapped by surface OH groups,  $\nu_{1/2}$  will increase due to the restriction of their diffusion. The continuous increase of  $\nu_{1/2}$  for  $\theta < 1$  with decreasing temperature suggests that the motional mode forgiven for  $\theta > 1.3$  is quenched or forbidden in the first layer even at room temperature, e.g., as being so if the motion for  $\theta$ > 1.3 is vertical diffusion to the wall.

The motion responsible for  $T_1$  at  $\theta > 1.3$  would be different from the motion for  $\theta < 1$ , considering the difference in the temperature dependence of  $T_1^{-1}$ . We suppose that the motion for  $\theta > 1$  may be lateral diffusion (Figure 6C). It was reported that a correlation time of translation,  $\tau_{\rm trans},$  for water adsorbed on wide pores of silica gel was on the order of  $10^{-10}$  s. However, in the alunite having slitlike micropores of 1.0-nm width, water molecules in the second layer make hydrogen bonds with those adsorbed on both walls, and thus, the hydrogen-bonding water will be more difficult to move than those in the pores of the silica gel. Consequently,  $\tau_{\text{trans}}$  for water in the micropores of alunite would be much more than  $10^{-10}$  s, as estimated by the BPP theory.

The larger mobility of water in a bilayer than in a monolayer may arise from small  $\tau$  and/or an increase of the degree of freedom of motion, e.g., the vertical diffusion to walls that cannot exist in a monolayer. In addition, a certain motional mode in the bilayer was quenched by cooling to -30 °C, as suggested by the abrupt increase of  $\nu_{1/2}$  (Figure 6B). The magnitude of  $\nu_{1/2}$  and its temperature dependence for  $\theta = 1.4$  are almost the same as those for  $\theta = 1.9$ . This suggests that the states of water on the outer surfaces or in the intersticies between thin crystals are unchanged with θ.

It should be noticed that when monolayer is complete or when micropores are filled with water, the motional mode of adsorbed water seems to change from the rotation at low temperature to the diffusion in the region about -25 °C, as seen in the curve for  $\theta = 1.1$  in Figure 6C.

Dielectric Relaxation Mechanism. A maximum  $\tau_d$  value, 1.2  $\times 10^{-3}$ /s, of water on the porous alunite at  $\theta = 1.3$  and 30 °C was 600 times larger than the relaxation time of ice I, extrapolated to 30 °C.<sup>22</sup> The result indicates that water molecules in 1.3 layers are extremely immobilized and corresponds to ice I near -40 °C. The potential field from the walls of slitlike micropores stabilizes water adsorbed thereon to make the "cold" ice.

The  $\tau_{\rm d}$  values are much larger than  $\tau$  values, especially around  $\theta = 1.3$ . Thus, the motions detected by the NMR and dielectric relaxation methods should be different from each other, because  $\tau_d^{D} = 3\tau$ ,<sup>26b</sup> where  $\tau_d^{D}$  is the correlation time of Debye for the orientation of molecules with a permanent dipole moment. Such a slow motion as observed by the dielectric relaxation may not be detected by <sup>1</sup>H NMR because of other rapid motions.

We will interpret the peculiar variation of dielectric relaxation time in the following way. The trapped water in the center of the hexagonal, skeletal OH rings of alunite, which rotates freely, forms a small cluster in the monolayer to produce easily D and L orientational defects.<sup>29</sup> This may lead to the smaller  $\tau_d$  values for a monolayer on the porous alunite, smaller than those on hematite and silica gel.<sup>2,8</sup> The small water cluster grows with increasing  $\theta$ , the monolayer is completed at  $\theta = 1$ , and the cluster may become maximum (three water layers) at  $\theta = 1.3$  where the micropore of the alunite is filled with water. Then, the  $\tau_d$  value may be much longer than that of ice with the growth of a twodimensional cluster in slitlike micropores, as reported by Sack and Meakins,<sup>30</sup> who proposed that the relaxation time of a cluster of alcohol formed by hydrogen bonds depends strongly on the cluster size and may become more than  $10^{-2}$  s. Probably, the orientation process in the large cluster is disturbed by a water molecule in the second layer bridging between water molecules faced on each wall of the micropores through hydrogen bonds. At the same time, as the cluster grows, the interfacial polarization<sup>4</sup> (the Maxwell-Wagner mechanism<sup>31</sup>) may reduce the  $\tau_d$  value. After the micropores are filled with water, the interfacial polarization of the water layers on the outer surfaces and the intersticies between crystals as well as in the micropores becomes responsible for the dielectric relaxation. This would lead to the steep decrease of  $\tau_d$ with increasing  $\theta$ . Thus, the maxima in the  $\tau_d - \theta$  curves seem to appear at  $\theta = 1.3$ . The interfacial polarization is brought about through diffusion of water molecules or protons.

The activation energy of the dielectric relaxation, >0.3 eV for  $\theta < 0.9$  and ca. 0.22 eV for  $\theta > 1.3$ , is smaller than that (ca. 0.58 eV) of ice for the orientational process of four bonded molecules.<sup>22,32a</sup> Since the number of hydrogen bonds of a water molecule in a monolayer is less than four, the activation energy of the dielectric relaxation due to the orientational defects in the monolayer may be less than 0.58 eV, as in our case. If the dielectric relaxation for  $\theta > 1.3$  occurs by the Maxwell-Wagner mechanism, the activation energy of the relaxation would be comparable to that for an electric conduction.<sup>33</sup> Since the activation energy of bulk conductivity for ice<sup>32b</sup> and water layers adsorbed on  $\gamma$ -FeOOH<sup>34</sup> and TiO<sub>2</sub><sup>4a</sup> are 0.35, <0.3, and 0.27 eV, respectively, it is likely that the interfacial polarization is responsible for the dielectric relaxation at  $\theta > 1.3$ .

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Registry No. H<sub>2</sub>O, 7732-18-5; KAl<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>, 12253-07-5; alunite, 1302-91-6.

<sup>(29)</sup> Fletcher, N. H. The Chemical Physics of Ice; Cambridge University Press: London, 1979; Chapters 7 and 9.

<sup>(30)</sup> Meakins, R. J.; Sack, R. A. Aust. J. Sci. Res. 1951, A4, 213. Sack, R. A. Ibid. 1952, A5, 135.

<sup>(31)</sup> For example: Oka, S.; Nakata, O. Kotai Yudentai-Ron (Theory of Solid Dielectrics); Iwanami: Tokyo, 1964; p 80. van Beek, L. K. H. Prog. Dielectr. 1967, 7, 69.

<sup>(32) (</sup>a) Hasted, J. B. In *Water*; Franks, F., Ed.; Plenum: New York, 1972; Vol. 1, p 255.
(b) Franks, F. In Referance 32a; p 115.
(33) Kamiyoshi, K.; Odake, T. J. Chem. Phys. 1953, 21, 1295.

<sup>(34)</sup> Kaneko, K.; Inouye, K. Bull. Chem. Soc. Jpn. 1979, 52, 315.