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Calorimetric study of water two-dimensionally condensed on the homogeneous surface of a solid ☆

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Abstract

The state of water adsorbed on ZnO, Cr_2O_3 and SrF_2, on which two-dimensional condensation of water occurs, has been studied by a direct calorimetric method. It was found that the differential heat of adsorption exhibits a maximum in the coverage region where a steep increase in the adsorbed amount is observed in the corresponding adsorption isotherm. This suggests the two-dimensional condensation of water due to the strong lateral interaction between water molecules adsorbed on the homogeneous surface in addition to their interaction with the underlying surface. The entropy change for the adsorbed water during the adsorption process, $-\Delta S_{\text{ads}}$, can be estimated from the heat and isotherm data, and compared with the theoretical values. As a result, it was revealed that the localized adsorption of water molecules occurs on the homogeneous surfaces of ZnO, Cr_2O_3 and SrF_2 at 301 K. By applying Fowler's equation, which can be applicable to the localized monolayer adsorption on the homogeneous surface with interactions among the adsorbed molecules, to the present systems and by separating the experimental adsorption isotherm into two components, the adsorptions on the heterogeneous surface and on the homogeneous one, the interaction energies for both types of interactions were evaluated; the lateral interaction energies were 8.8, 9.8 and 8.2 kJ mol^{-1} for ZnO, Cr_2O_3 and SrF_2, and the adsorbate–adsorbent interaction energies were 46, 55 and 58 kJ mol^{-1}, respectively. These results are

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interpreted in terms of the difference in the structure of these solid surfaces. The adsorbed state of water is also discussed through a dielectric study.

Keywords: Adsorption; Direct calorimetry; Homogeneous surface; Surface; Water

1. Introduction

Surfaces of solids, especially metal oxides, usually terminate in breaking of the chemical bonds and hence are covered with surface hydroxyl groups produced by contact with moist air. Such surfaces carry both donor and acceptor groups for the formation of hydrogen bonding. This hydrogen-bonding interaction plays a dominant role in practical processes such as corrosion and catalytic reactions [1-3]. We have found such an anomalous phenomenon that a distinct step appears in the adsorption isotherm of water vapor on some kinds of solid surfaces [4-6]. This has been ascribed to the two-dimensional condensation of water molecules resulting from their lateral interactions on the homogeneous surface of the solid. Therefore, it is very interesting and important to have a fundamental understanding of the properties of water layers formed on such solid surfaces.

In the present study, the state of two-dimensionally condensed water on the solid surface is discussed from the thermodynamic considerations and dielectric behavior.

2. Experimental

The ZnO sample used in the present study was Kadox 25 from New Jersey Zinc Co. The Cr_2O_3 sample was obtained by the decomposition of $Cr_2(C_2O_4)_3 \cdot 6H_2O$ at 873 K, and the SrF_2 sample was prepared by precipitation on mixing aqueous solutions of $Sr(NO_3)_2$ and NH_4F. The specific surface areas obtained by N_2 adsorption at 77 K were 8.15, 12.0 and 25.6 $m^2\ g^{-1}$ for ZnO, Cr_2O_3 and SrF_2, respectively.

The adsorption measurements were carried out using a conventional volumetric adsorption apparatus and the heat of adsorption of water vapor on these samples were determined by direct calorimetry. The adsorption calorimeter used was an adiabatic type and its details have been described elsewhere [7,8]. First, simultaneous measurements of the heat of adsorption and the adsorption isotherm were performed at 301 K for the sample which had been pretreated at 723 K under a reduced pressure of 1.3 mPa (first adsorption). After these measurements, the sample was exposed to saturated water vapor at 301 K for 12 h to promote surface hydration, followed by degassing at 301 K to remove weakly physisorbed water. Then, the second adsorption measurement was performed again at 301 K (second adsorption).

Dielectric permittivity and loss were measured in the frequency range from 0.1 to 5 MHz and at various temperatures, 298, 273, 221, 201, 179 and 159 K, by using impedance bridges, TR - 4 and TR - 10C (Ando Electric Co.). The detailed procedure of this measurement will be described elsewhere [9].

3. Results and discussion

The differential heats of adsorption and isotherms for water vapor on the ZnO, Cr_2O_3 and SrF_2 samples pretreated at 723 K are shown in Fig. 1. In the first adsorption on ZnO and Cr_2O_3, the higher adsorption heats, about 170 and 160 kJ mol^{-1} respectively, decrease initially with increasing amount adsorbed, followed by an appearance of small plateau of about 150 kJ mol^{-1} in the adsorption range from 0.025 to 0.075 cm^3 m^{-2}. Then the adsorption heats decrease steeply to give the second plateau with a small maximum (approx. 46 kJ mol^{-1} for ZnO and 60 kJ mol^{-1} for Cr_2O_3), and finally reach the value of the heat of liquefaction of water vapor. The regions where these second plateaus appear in the adsorption heats, from 0.25 to 0.35 cm^3 m^{-2} for ZnO and from 0.15 to 0.25 cm^3 m^{-2} for Cr_2O_3, are in good agreement with those where the adsorbed amount increases steeply to give rise to a step in the adsorption isotherm. The differential heat curves for the second adsorption on these

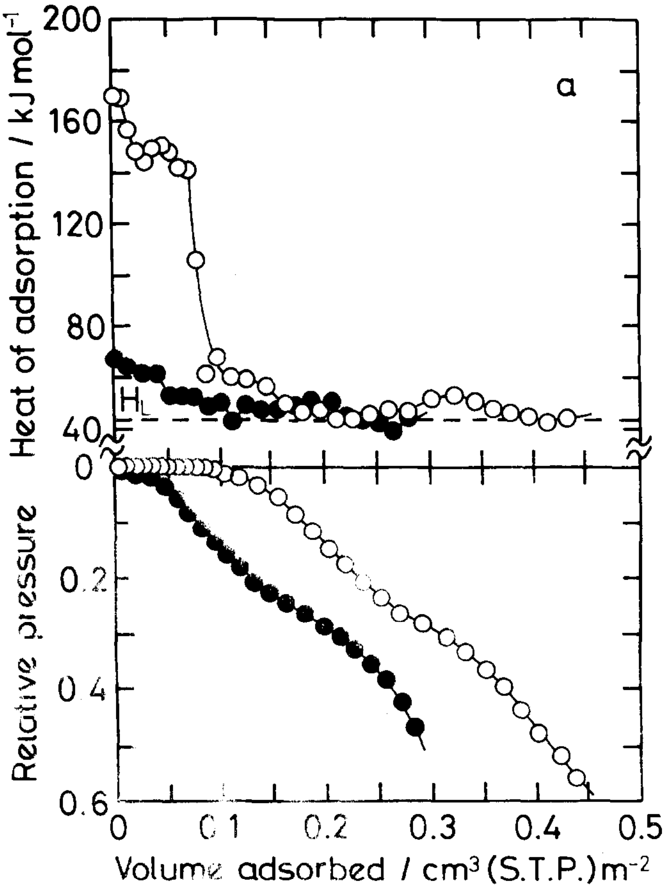

Fig. 1(a)

samples resemble notably those for the first adsorption, except for having no large adsorption heat in the initial stage; both the heat curve and isotherm for the second adsorption appear to be shifted to lower pressure or a smaller adsorbed amount. The extent of this shift may correspond to the chemisorbed amount.

The first and second adsorption isotherms are almost in parallel over the entire range of equilibrium pressures examined and the amount adsorbed is much larger in the first adsorption process than in the second. The initial high heats for ZnO and Cr_2O_3 can be related to a steep increase in the adsorbed amount along the ordinate axis in the isotherm, which suggests a rapid chemisorption of water at the lower pressures. The observed high heat, above 140 kJ mol^{-1} for ZnO and Cr_2O_3, obviously indicates the dissociative chemisorption of water. Fubini et al. [10] have also reported that the heat of dissociative adsorption of water exceeds 140 kJ mol^{-1}. It should be noted that the plateau in the heat curve appears in the initial region, even in the first adsorption process; this is definitive evidence for the existence of an energetically homogeneous surface on these oxides.

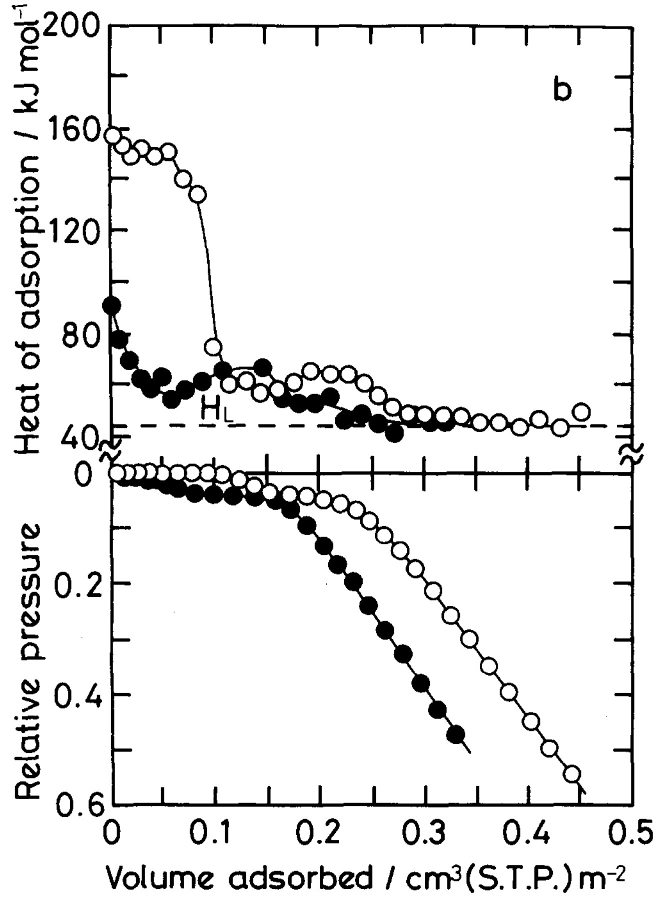

Fig. 1(b)

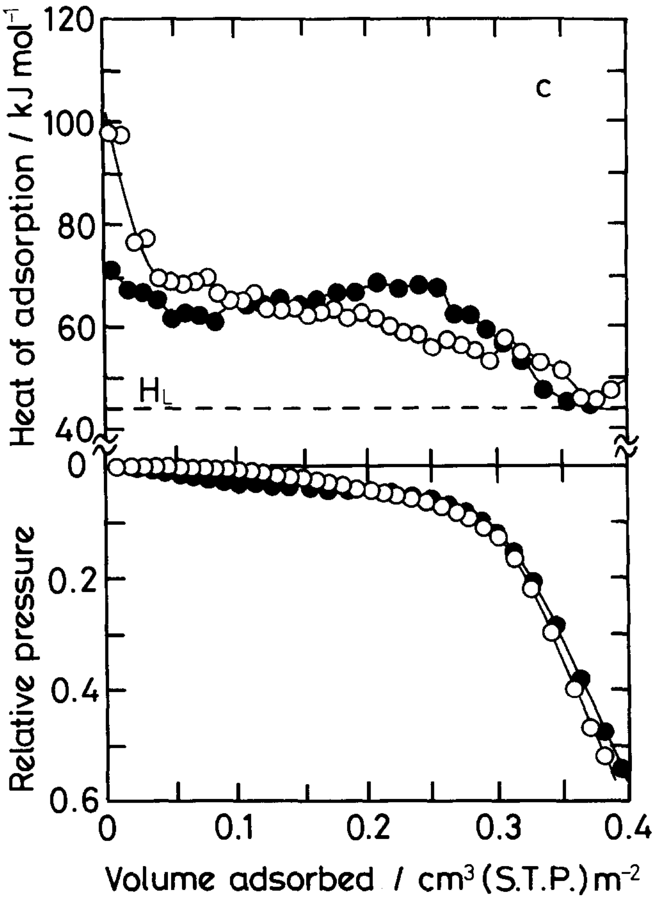

Fig. 1. Differential heat of adsorption and the adsorption isotherm for water vapor on (a) ZnO, (b) Cr_2O_3 and (c) SrF_2 at 301 K. Open and filled circles represent the first and second adsorptions, respectively. H_L denotes the heat of liquefaction of water.

However, the heat of adsorption on SrF_2 is 98 kJ mol^{-1} at the initial stage and decreases abruptly to 70 kJ mol^{-1} and then monotonously with increasing coverage, which is distinct from the cases of ZnO and Cr_2O_3. The shape of the adsorption isotherm is also different from those for ZnO and Cr_2O_3; the steep rise of the adsorption isotherm is more distinct and the first and second adsorption isotherms are not parallel to each other. The amount adsorbed in the first adsorption process is larger than that in the second in the lower pressure region, and this situation is reversed when the pressure exceeds a moderate value. A similar phenomenon has been observed and ascribed to a slow chemisorption of water in the first adsorption process [11]. Another distinct feature in the adsorption of water on SrF_2 is the absence of a plateau on the heat curve in the lower coverage, which may be indicative of the presence of a heterogeneous surface or of slow, incomplete surface hydration. High pressure and long duration of contact with water vapor may be needed to promote surface hydration on this sample. The smaller values of adsorption heat in the lower coverage compared with those for metal oxides suggests a different state for surface hydration, i.e. molecular adsorption rather than dissociative adsorption of water [11].

The heat of adsorption curves for the second adsorption on these three samples exhibit a similar tendency; the heats of adsorption of water on ZnO, Cr_2O_3 and SrF_2 are 70, 90 and 70 kJ mol^{-1} at the initial stage, respectively, and then they decrease with increasing amount of adsorbed water. When the monolayer of water is completed, the heats settle down to the level of heat of liquefaction of water vapor. The adsorption heat in the region where the step appears in the isotherm gives almost the same values of 65 and 66 kJ mol^{-1} for Cr_2O_3 and SrF_2, respectively, but a much smaller value of 48 kJ mol^{-1} for ZnO. The appearance of a maximum in the heat curve suggests a strong lateral interaction among the adsorbed water molecules, corresponding to the appearance of a step in the adsorption isotherm.

The evaluation of the integral molar entropy of adsorption serves to elucidate the adsorption phenomena in more detail. Because the second adsorption process is a reversible one, the thermodynamic treatment is a possible approach in the investigation of the state of water adsorbed on these solid surfaces. The entropy change during the adsorption process, ΔS_{ads}, can be evaluated from the calorimetric and isotherm data by applying the equation [12]

$$-\Delta S_{\mathrm{ads}} = S_{\mathrm{g}}^{\ominus} - S_{\mathrm{s}} = R\ln(p/p^{\ominus}) + (Q'/T) - (R/V)\int_0^v V\,\mathrm{d}(\ln p) \tag{1}$$

where $S_{\mathrm{g}}^{\ominus}$ is the standard molar entropy of the gas phase (water vapor), S_{s} the molar entropy of the adsorbed phase, Q' the molar integral enthalpy of adsorption, V the adsorbed amount, and p and $p^{\ominus}$ are the equilibrium and standard pressures, respectively.

Fig. 2 shows the entropy change during adsorption of water vapor on the fully hydroxylated solid surfaces, i.e. the second adsorption process. The entropy change obtained for ZnO, -140 J K^{-1} mol^{-1} in the lower coverage region, decreases monotonously to -120 J K^{-1} mol^{-1} near the completion of the monolayer. This value is comparable to the entropy change accompanying the phase change from water vapor to liquid water. However, $-\Delta S_{\mathrm{ads}}$ for water adsorbed on SrF_2, 160 J K^{-1} mol^{-1} at the initial stage, decreases to 145 J K^{-1} mol^{-1}, and then increases, passing through a maximum in the coverage range from 0.3 to 1.0, and again decreases to 145 J K^{-1} mol^{-1}. Similar behavior in entropy change is observed for the adsorbed water on Cr_2O_3, though the maximum is not so large as in the case of SrF_2. The increase in $-\Delta S_{\mathrm{ads}}$ is observed in the surface coverage between 0.5 and 1.0, corresponding to the region where the step appears in the adsorption isotherm. The appearance of a maximum in $-\Delta S_{\mathrm{ads}}$ can be interpreted as the adsorbed water molecules interacting laterally without migration on the solid surface. The formation of an ice-like structure or the occurrence of a strong lateral interaction, as well as the adsorbent–adsorbate interaction, will result in $-\Delta S_{\mathrm{ads}}$ becoming increasingly

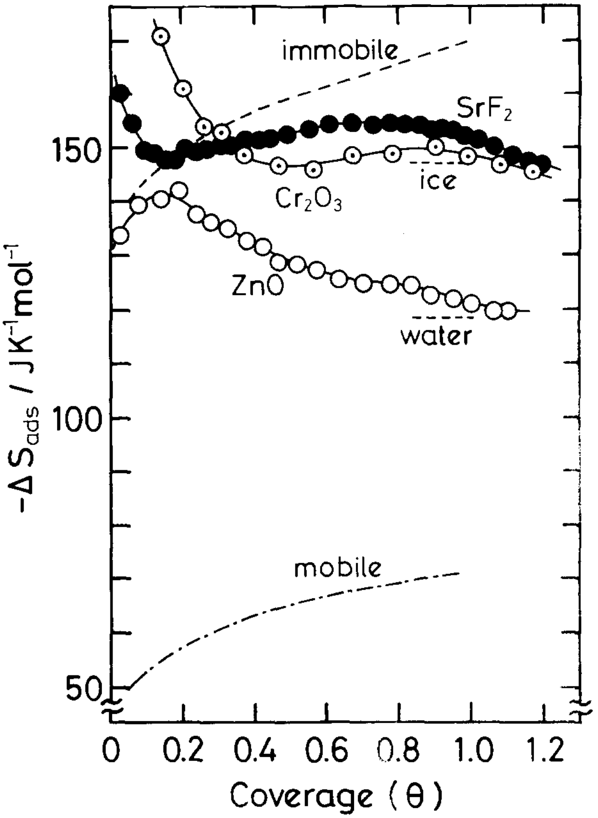

Fig. 2. Integral molar entropy change during adsorption of water vapor on the fully hydroxylated solid surfaces: ○, ZnO; ⊙, Cr_2O_3; ●, SrF_2. Entropy changes for the Cr_2O_3-H_2O system are also evaluated assuming immobile and mobile films.

negative. Indeed, the values of $-\Delta S_{ads}$ for the Cr_2O_3-H_2O and SrF_2-H_2O systems at the monolayer coverage are comparable to the entropy change accompanying the phase change from water vapor to ice as shown in Fig. 2.

The entropy change can also be estimated from the statistical considerations [13-16]. As a typical example, for the Cr_2O_3-H_2O system the entropy change was evaluated by assuming an immobile (localized) film and a mobile (delocalized) film as extreme cases, and the results are also shown in Fig. 2. From a comparison of the experimental values with the theoretical ones, it is found that water molecules adsorbed on Cr_2O_3 or SrF_2 are in a localized state, whereas those on ZnO are intermediate between the immobile and mobile states.

In connection with the above discussion, we can estimate the lateral interaction energy by applying Fowler's equation which expresses a localized adsorption on the homogeneous surface [17]

$$Y = \ln[\theta/(1-\theta)] - \ln p = [c\omega/(RT)]\theta - \ln K \qquad (2)$$

where K is a constant, $c\omega$ represents the interaction energy among the adsorbed molecules, θ the surface coverage, and the remaining symbols have their usual meanings. If a large part of the surface is uniform in energy, an adsorption isotherm with no initial knee or distinct step will be obtained. However, if the surface is substantially heterogeneous, an adsorption isotherm in which the initial knee is developed, i.e. a type II isotherm in the BDDT classification [18], will be obtained. Experimental isotherms obtained in the present study seem to consist of both types of isotherms, and hence they can be separated into two parts: for heterogeneous and for homogeneous surfaces. The procedure of separating the experimental isotherm is as follows. First, the adsorption isotherm for the heterogeneous surface can be obtained by extending the initial part of the measured isotherm involving a knee with the aid of the BET equation [19], and then it is subtracted from the measured isotherm to give the isotherm for the homogeneous surface. These separated isotherms, as a typical example for the second water adsorption on Cr_2O_3, are illustrated in Fig. 3. As is seen from this figure, adsorption on the homogeneous surface is depressed in the lower pressure region and then increases sharply at a certain pressure. Fowler's equation can be applied to the isotherm for the homogeneous surface and the results are shown in Fig. 4. The plots of Y against

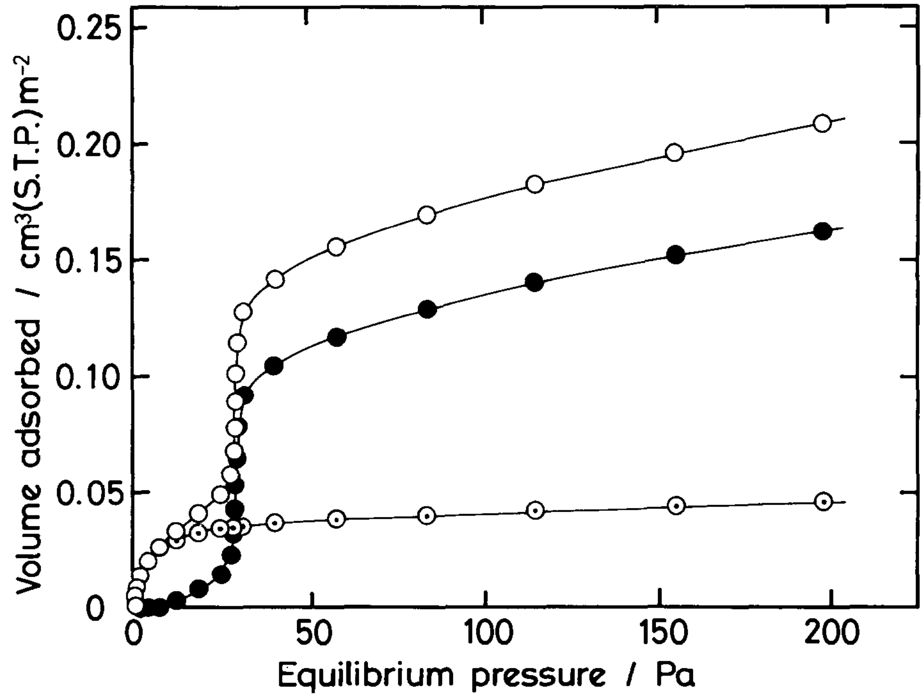

Fig. 3. Analysis of the adsorption isotherm for water vapor on Cr_2O_3. The experimental isotherm (○) is separated into two isotherms: adsorption on the heterogeneous surface (⊙) and on the homogeneous surface (●).

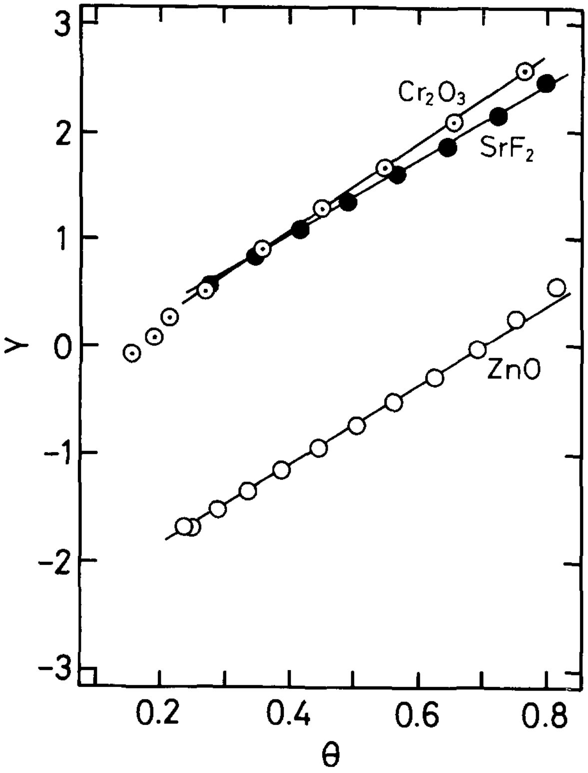

Fig. 4. Application of Fowler's equation to the adsorption isotherm for the homogeneous surface: ○, ZnO; ⊙, Cr_2O_3; ●, SrF_2.

θ give a straight line in the coverage range of about 0.3–0.7 with $c\omega$ values of 9.8, 8.8 and 8.2 kJ mol^{-1} for Cr_2O_3, ZnO and SrF_2, respectively. These values obtained for the lateral interaction energy, mostly two-dimensional hydrogen-bonding energy, are smaller than the value for the three-dimensional bulk water, i.e. 12 kJ mol^{-1} [20]. The lateral interaction energy of water molecules is stronger on the Cr_2O_3 surface than on the SrF_2 surface. Taking into account the fact that water molecules on the SrF_2 surface form a bent hydrogen-bonding and have constrained structure [16], it may be possible to consider that the water molecules form an ice-like structure on the Cr_2O_3 surface. On the ZnO surface, water molecules interact moderately with each other. The differential heat curve shows a raised plateau in the region corresponding to the two-dimensional condensation on the isotherm, and the height of the plateau above the general level resulting from the interaction of adsorbate molecules with the homogeneous solid surface corresponds to the lateral interaction energy [21]. Because this additional energy due to the lateral interaction is involved in the total interaction energy obtained experimentally, we can estimate the net interaction energy between the adsorbed species and the surface by eliminating the lateral interaction energy from the total energy. As a result, it was found that the surfaces of both Cr_2O_3 and SrF_2 are homogeneous with adsorption energies of about 55 and 58 kJ mol^{-1}, respectively, for water molecules. These values are much larger than the value of 46 kJ mol^{-1} for the $ZnO-H_2O$ system, indicating that the adsorbed water molecules interact more strongly with the surface of Cr_2O_3 or SrF_2 than with the ZnO surface.

Fowler's equation for the completely localized monolayer adsorption can be derived from statistical considerations and is given by [22]

$$p = (8\pi^3 m^3 v_x{}^2 v_y{}^2 v_z{}^2/kT)^{1/2} \exp(\varepsilon_{\min}/kT)[\theta/(1-\theta)] \exp(c\omega\theta/kT) \tag{3}$$

where $\varepsilon_{\min}$ denotes the minimum energy of the adsorption potential, v_x, v_y and v_z are the vibrational frequencies along the x, y and z axes, respectively, and the remaining symbols have the same meanings as in Eq. (2) or their usual meanings. This equation implies that the step on the adsorption isotherm appears at lower pressure as the interaction energy increases, which agrees with the results obtained above; the pressure at which the step appears falls in the order SrF_2, Cr_2O_3, and ZnO. We can calculate the averaged value of v by putting $v_x = v_y = v_z$ and by introducing both values of $\varepsilon_{\min}$ and $c\omega$, where $\varepsilon_{\min}$ is assumed to be the interaction energy between the adsorbed molecule and the homogeneous solid surface, and $c\omega$ is taken as the value obtained by Eq. (2). As a result, the values of v are estimated to be 4×10^{12} s^{-1} for SrF_2, 3×10^{12} s^{-1} for Cr_2O_3 and 1.5×10^{12} s^{-1} for ZnO, which are in good agreement with that proposed by Fripiat et al. [14]. These values correspond to the translational mode of water molecules in ice or liquid water [20], indicating that the adsorbed water molecules have moderate interactions with the underlying surface.

The dielectric losses, ε'', at various temperatures are plotted against the frequency for the $Cr_2O_3-H_2O$ and SrF_2-H_2O systems (at a surface coverage of 0.55) in Fig. 5. The frequency at which ε'' exhibits a maximum corresponds to a characteristic frequency (f_m) for the observed dielectric dispersion. A large relaxation is observed in the lower frequency region at 298 K: 0.1 Hz for Cr_2O_3 and 1 Hz for SrF_2. As the temperature is lowered, the relaxation shifts to lower frequencies and the ε'' value becomes smaller. In the case of SrF_2, a new relaxation appears in the higher frequency region and at temperatures below 201 K. Similar results have been reported for ZnO by Iwaki and Morimoto [23]; the large relaxation observed around 300 Hz and at 273 K has been assigned to the interfacial polarization arising from a heterogeneity of the system and the relaxation observed at lower temperatures to the orientational polarization of the adsorbed water molecules. According to their proposal, we can assign these relaxations observed for the SrF_2-H_2O system to the interfacial and orientational polarizations of physisorbed water, respectively. However, the relaxation observed for the $Cr_2O_3-H_2O$ system at 298 K may be attributed to the interfacial polarization, though no relaxations are observed at lower temperatures. When we examine the ε'' data more carefully, a discernible shoulder can be found at about 300 Hz and this shifts to lower frequencies with decreasing temperature. This shoulder could not be recognized for the sample with zero coverage, but became pronounced for the samples with increasing coverage. Therefore, such a shoulder is explained as a dipolar polariza-

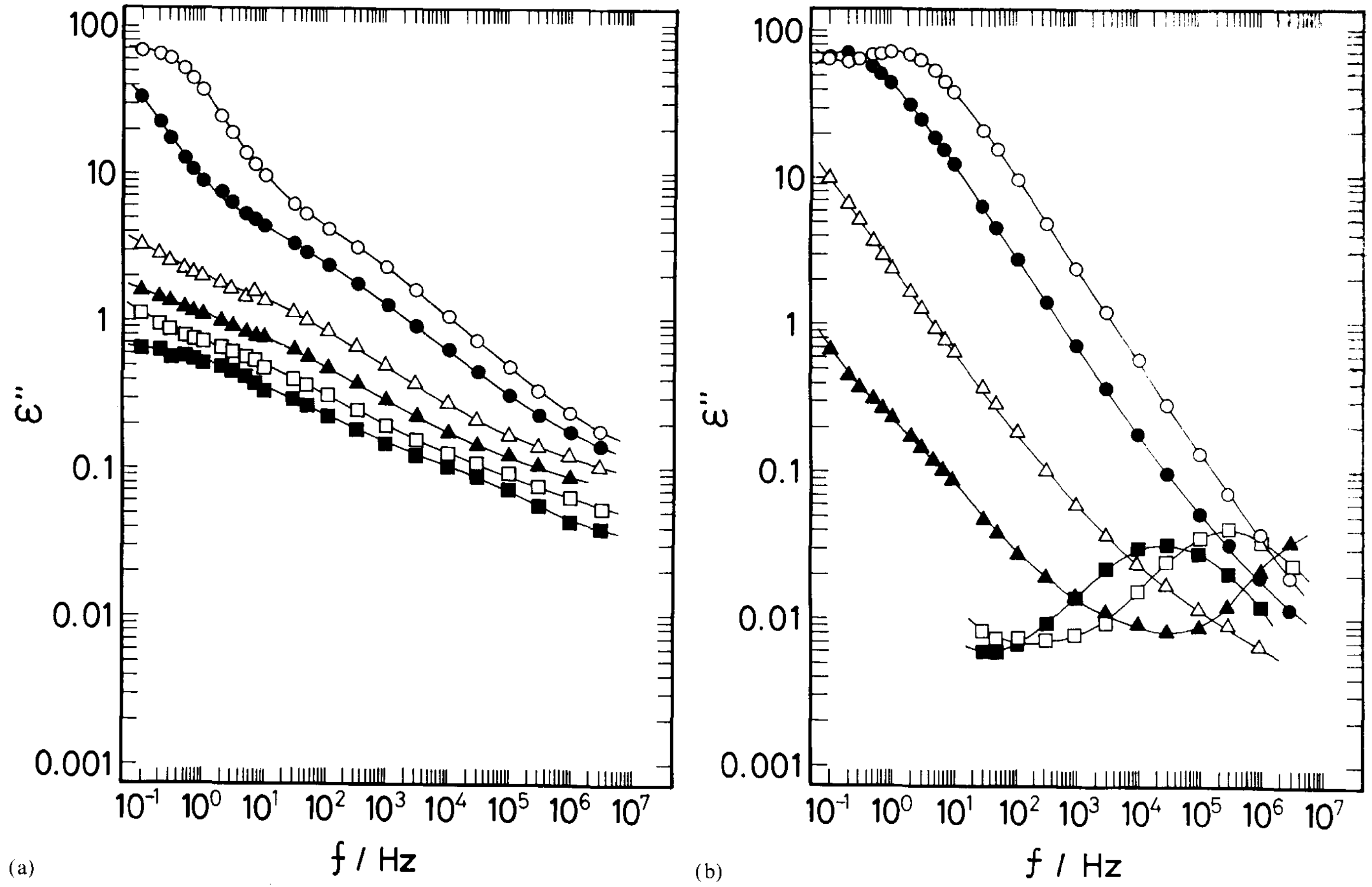

Fig. 5. Variation of dielectric loss (ε'') with frequency for adsorbed water on (a) Cr_2O_3 and (b) SrF_2 at various temperatures: ○, 298; ●, 273; △, 228; ▲, 201; □, 179; ■, 159 K.

tion of the adsorbed water. With reference to the relaxation frequencies for ice and liquid water of 2.5 kHz at 273 K [24] and 18 GHz at 293 K [25], respectively, the observed relaxation at 300 Hz and at 298 K for the Cr_2O_3–H_2O system is attributable to the relaxation resulting from the adsorbed water. Consequently, these dielectric data lead us to conclude that the adsorbed water on Cr_2O_3 is in an ice-like state and the water on SrF_2 and ZnO is in a more mobile state or liquid state, in accordance with the calorimetric results.

4. Conclusions

From the present study on the state of water adsorbed on ZnO, Cr_2O_3 and SrF_2 surfaces, the following conclusions can be derived. Water molecules adsorbed on the fully hydroxylated surfaces of ZnO, Cr_2O_3 and SrF_2 exhibit a strong lateral interaction as well as a strong interaction with the underlying surface; the interaction energies of the former type are 8.8, 9.8 and 8.2, and those of the latter type are 46, 55, 58 kJ mol^{-1} for ZnO, Cr_2O_3 and SrF_2, respectively. The water molecules adsorbed on the Cr_2O_3 surface are in the localized state with an ice-like structure and those on the SrF_2 surface are also in the localized state but with a less rigid or nearly amorphous structure. On the ZnO surface, water molecules are rather mobile compared with the other two cases, and they are assumed to be in the liquid state. The physisorbed water on the Cr_2O_3 and SrF_2 surfaces can interact strongly with surface hydroxyl species, while water on the ZnO surface cannot interact so strongly with surface hydroxyl groups. The structure of the hydroxyl layer formed on the solid surface, especially on the homogeneous solid surface, affects the state of the two-dimensionally condensed water.

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