THE INTERACTION OF WATER WITH GOETHITE (α-FeOOH) AND AMORPHOUS HYDRATED FERRIC OXIDE SURFACES*

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Abstract—The interaction of water with synthetically prepared goethite (α-FeOOH) and amorphous hydrated ferric oxide surfaces was studied using i.r. absorption and water vapor adsorption measurements. I.R. results show that the last traces of physically adsorbed water are removed from the amorphous material by outgassing at 25°C. In contrast, goethite retains approximately a monolayer of physically adsorbed water with similar outgassing. This monolayer of water on goethite, which is presumably hydrogen-bonded at least in part with structural hydroxyls, is readily exchangeable with D_2O.

Integral entropies of adsorption were evaluated from water vapor adsorption isotherms at 15, 25 and 35°C and compared with values for mobile and immobile layers calculated through application of statistical mechanics (McCafferty and Zettlemoyer, 1970). Entropy values for both the first physically adsorbed monolayer of water on the amorphous material and the second monolayer on goethite were about the same as or greater than those calculated for an immobile layer, indicating strong hydrogen bonding of water by both surfaces. The larger deviation between the entropy values for goethite and those calculated for the immobile layer may be associated with changes in the structure of the first as well as the second physically adsorbed water layers. Surface areas, calculated using the BET method, were 320 and 32 m² g⁻¹ for the amorphous material and goethite respectively. Since the unit surface activity is probably about the same for the two materials, it follows that as the amorphous material crystallizes to form goethite, there would be a reduction in total surface activity in proportion to the reduction in surface area.

INTRODUCTION

Previous studies have shown that amorphous hydrated ferric oxide may crystallize to form goethite (Mackenzie and Meldau, 1959; Sims and Bingham, 1968; Smith and Kidd, 1949; Landa and Gast, 1973), or hematite (Milligan, 1952) or both (Schwertmann *et al.*, 1949). All three of these materials occur naturally in soils and sediments, and may contribute significantly toward their surface behavior. For example, Blyholder and Richardson (1962) and Jurinak (1964) have shown that the acidity of the first physically adsorbed water on hematite is sufficient to protonate NH_3 and N-butylamine to form NH_4^+ and N-butyl-ammonium ions respectively. In addition, Jurinak (1964) found that the surface acidity of goethite was somewhat greater than

for hematite, which he attributed to the presence of the proton in the α-FeOOH structure.

The properties of adsorbed water on hematite, responsible for its surface activity, have been extensively studied (Blyholder and Richardson, 1962; McCafferty and Zettlemoyer, 1970). However, much less is known about the properties of adsorbed water on goethite and amorphous hydrated ferric oxide.

We have shown that a hydrated ferric oxide precipitate, amorphous to X-ray diffraction, infrared absorption, and pH 3·0 ammonium oxalate extraction can be prepared by the addition of ferric chloride to KOH (Landa and Gast, 1973). As little as 2 per cent crystallinity in the amorphous precipitate can be detected by the three methods mentioned above. This precipitate, which remains amorphous for extended periods of time if maintained at low pH (< 7·0) and low temperature, crystallizes to goethite (α-FeOOH) within a few hours when adjusted to high pH (> 12·0) and temperatures of 60°C or above. Since the conversion to goethite is essentially complete, the procedure provides a means for preparing samples of amorphous and crystalline (α-FeOOH) hydrated ferric oxides sufficiently

stable for laboratory study. The purpose of the study reported here was to examine the surface area and water adsorption properties of these synthetically prepared materials.

EXPERIMENTAL

Preparation of synthetic hydroxy-iron materials

The synthetic, amorphous, hydrated ferric oxide gel was prepared by dropwise addition of an equivalent amount of ferric chloride to 250 ml of 2·0 N KOH while stirring rapidly. The flocculated dark reddish–brown precipitate was washed with deionized water by centrifuging and decantation until it began to disperse. For water adsorption studies, a portion of the amorphous precipitate, which had a pH of about 7, was evaporated to dryness at room temperature and ground to pass through a 60 mesh sieve. The remaining portion of the gel was adjusted to pH 12·0 with KOH and aged at 60°C to form goethite, which was air-dried and ground to pass a 60 mesh sieve. The materials were tested for the presence or absence of crystallinity by the pH 3·0 ammonium oxalate method before and intermittently during the water adsorption studies.

I.R. analysis

About 5 mg of goethite or amorphous hydrated ferric oxide were applied from aqueous or ethanol suspension to a 2·5 cm dia. Irtran-2 (Eastman Kodak) disk and allowed to air-dry. The disk was mounted into a high vacuum (about 10^{-6} mm Hg) i.r. cell having NaCl windows and analyzed using a Beckman model i.r.-12 spectrophotometer operated in the double beam mode. To minimize scattering and refractive index effects, samples for infrared analysis should be ground to a particle size below the wavelength of the radiation used. Thus, for the Itran-2 transmission range, the particles should be reduced to less than 2 μm. Since electron micrographs reveal the goethite crystals to be about 1 μm in length (Landa and Gast, 1973), no grinding was required. A sample of the air-dried amorphous material was ground with a glazed mortar and pestle for about 10 min under absolute ethanol to achieve the desired particle size.

Water vapor adsorption–desorption isotherms

Water vapor adsorption–desorption isotherms were determined with a conventional gravimetric vapor adsorption apparatus employing mechanical- and oil-diffusion vacuum pumps, a high precision McLeod gauge for measuring absolute pressures, and a quartz spring balance for determining the weight of water adsorbed. Water vapor pressure was measured with an oil manometer containing Apiezon-B oil with a density

15·4 times less than mercury. Equilibrium vapor pressures were determined to ± 0.1 mm oil or ± 0.006 mm Hg using a cathetometer. Variations in sample weight were determined to about ± 0.03 mg using a cathetometer on the quartz spring balance. Sample sizes of goethite or amorphous hydrated ferric oxide used ranged from 75 to 100 mg. Isotherms were determined at 15, 25 and 35°C with sample temperatures maintained at ± 0.1°C using a water jacket on the quartz spring balance and a circulating water bath. Samples were evacuated to constant weight before starting the adsorption measurements. This procedure required a few hours for geothite, but about 2 days for the amorphous material. Approximately 30 min were allowed between points on the isotherms although there was no detectable weight change after 15 min. At least two duplicate isotherms were run at each temperature to assure reproducibility of the results. In all cases, the samples returned to their original weight at the end of the desorption isotherms.

Evaluation of entropies of adsorption

The primary concern of this investigation was to determine the nature and degree of randomness of water molecules adsorbed on surfaces of goethite and amorphous hydrated ferric oxide. Therefore, integral, rather than differential, entropies of adsorption were determined, since the integral values can be directly taken as a measure of the randomness of the adsorbed molecules. These integral entropies of adsorption, ΔS(ads.) were evaluated at constant spreading pressure, ϕ, using the following expression (McCafferty and Zettlemoyer, 1970; Hill, 1950, 1951):

$$\left(\frac{\partial \ln p}{\partial T}\right)_\phi = -\frac{\Delta S\text{(ads.)}}{RT}. \tag{1}$$

The spreading pressure, ϕ, or decrease in surface free energy is given by the Gibbs equation:

$$\phi = RT \int_{p=0}^{p=p_0} \Gamma \, d \ln p \tag{2}$$

where Γ is the surface concentration of adsorbate expressed as moles per unit area. Writing $d \ln P = (1/p) \, dp$, equation (2) can be written as:

$$\phi = \frac{RT \, 10^{16}}{N \, n_0 \, 10\cdot 8} \int_0^{p_0} \frac{n}{p} \, dp \tag{3}$$

where n is the mg of water adsorbed per g of adsorbent, n_0 the mg of water per g in a monolayer, N Avogadro's number and 10·6 the cross-sectional area of the water molecule in A^2 (McCafferty and Zettlemoyer, 1970).

Finally, equation (3) can be reduced to:

$$\phi = \frac{0.1303\,T}{n_0} \int_0^{p_0} \frac{n}{p}\,\mathrm{d}p \qquad (4)$$

with ϕ expressed in ergs per cm^2. This integral can be evaluated graphically from plots of n/p vs p, but since n/p is largest for the smallest values of p, the isotherm must be determined very accurately at low pressures. This effect is illustrated in Fig. 1 which shows a plot of n/p vs p for water adsorption on goethite at 25°C. Alternately, as McCafferty and Zettlemoyer (1970) have illustrated, this integral can be evaluated analytically, employing the Dubinin–Radushkevich equation for describing the isotherm in the monolayer region and the modified Frenkel–Halsey–Hill equation in the multilayer region. As these authors have pointed out, the analytical approach is potentially more accurate than the graphical integration since the latter involves a judgement extrapolation of n/p to zero pressure. This uncertainty was minimized by using the oil manometer to obtain accurate measurements in the low pressure range. In addition, repeated measurements in this range insured accurate data. The uncertainty in the spreading pressures in the low pressure range was about two ergs per square centimeter.

RESULTS AND DISCUSSION

Nature of the adsorbing surfaces

When evaluating the water adsorption properties of a material such as goethite or amorphous hydrated ferric oxide it is necessary first to characterize the nature of the adsorbing surface. I.R. absorption spectros-
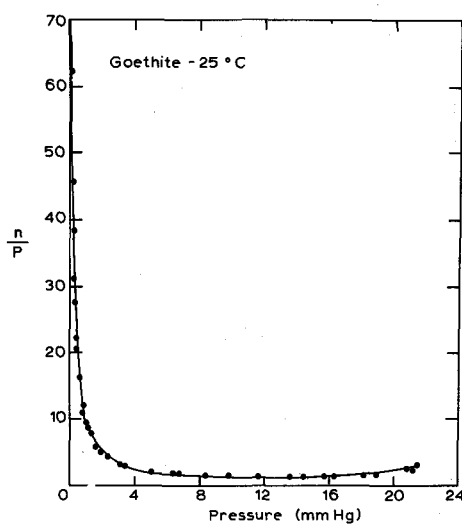

Fig. 1. Plot of n/p vs p in mm Hg for water vapor adsorption on goethite at 25°C.

copy is particularly useful in this regard. Using this procedure, Blyholder and Richardson (1962) have established that hematite (αFe_2O_3) surfaces outgassed at 25°C terminate in a layer of chemisorbed hydroxyl groups with little or no molecular water present. Temperatures up to 425°C are required to remove these remaining hydroxyls (Jurinak, 1964). In contrast, Yates (1961) found that the anatase (TiO_2) surface retains residual water when outgassed at 25°C, the last traces of which could only be removed by heating to 350°C. As in the case of hematite, a layer of chemisorbed hydroxyls remains on the surface after the last traces of molecular water are removed. These facts indicate that the first layer of physically adsorbed water is hydrogen bonded much more strongly to the hydroxyl surface of anatase than hematite. Jurinak (1964) attributes this difference to a stronger bond between Ti^{4+} and oxygen in anatase than between Fe^{3+} and oxygen in hematite, which results in a more mobile proton on the anatase surface and stronger hydrogen bonding with water.

The i.r. spectra of amorphous hydrated ferric oxide and goethite, both air dried and after extended evacuation at 10^{-6} mm mercury, are shown in Fig. 2. In the case of the amorphous material, the HOH bending vibration, at about 1630 cm^{-1} and the broad OH stretching vibration band for water at about 3350 cm^{-1}, present in the air-dried condition, were both removed by 24 hr evacuation. Due to the diffuse nature of the spectra, it was not possible to determine whether the evacuated surface terminates in chemisorbed hydroxyl as does hematite and anatase.

In contrast, significant quantities of residual water remain on the goethite surface after extended evacuation as evidenced by the absorption bands at 1630 and 3350 cm^{-1}. No change in these spectra could be observed after evacuation periods of up to 5 days at 10^{-6} mm Hg at room temperature. Apparently then, the first layer of water adsorbed on goethite is hydrogen bonded more strongly than in the case of either hematite or amorphous hydrated ferric oxide. This difference is probably related to the presence of the structural proton in the α-FeOOH structure.

The water adsorbed on both goethite and the amorphous material is readily exchangeable with D_2O as shown in Figs. 3 and 4. In each case, the samples were mounted on Irtran-2 disks and placed in a vacuum desiccator containing a flask of D_2O. The desiccator was evacuated, and after 4 days the sample was removed and scanned. The 3350 and 1630 cm^{-1} peaks shifted by the expected factor of $1/1.37$ to about 2600 and 1200 cm^{-1} for both goethite and the amorphous material. There was only a slight shift in the 3150 cm^{-1} peak of goethite; this absorption is presumably the O–H stretching band for the structural hydroxyls. The
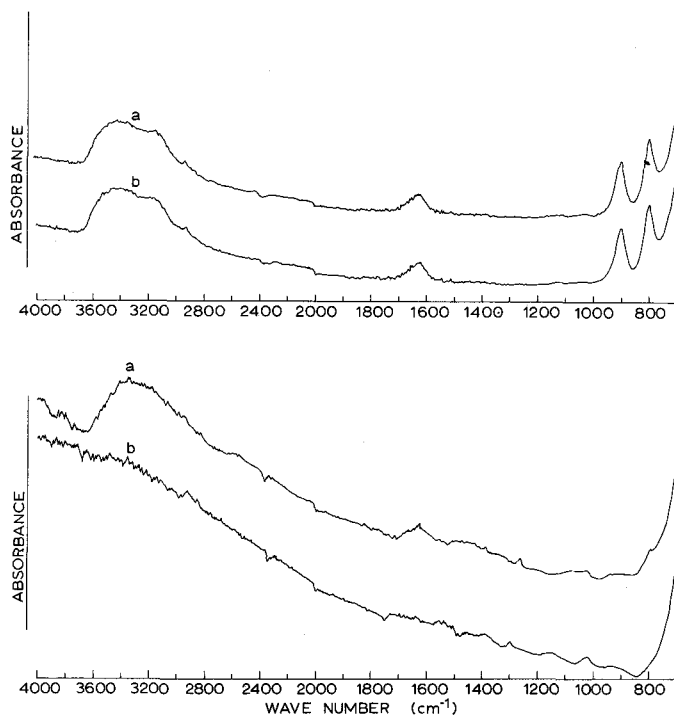
Fig. 2. I.R. absorption spectra of goethite (top) and amorphous hydrated ferric oxide (bottom) in (a) air dried and (b) after extended evacuation at 10^{-6} mm Hg.

vibrations at 795 and 890 cm^{-1} have been assigned to O–H bending vibrations for the structural hydroxyls (Marshall and Rutherford, 1971). However, it was not possible to follow shifts in these peaks on D$_2$O exchange since the 890 cm^{-1} peak shift is masked by

the existing 650 cm^{-1} peak, and the D$_2$O-shifted 795 cm^{-1} peak is outside the transmission range of Irtran-2. For both goethite and the amorphous material, the H$_2$O–D$_2$O exchange was reversible upon reexposure to water vapor.
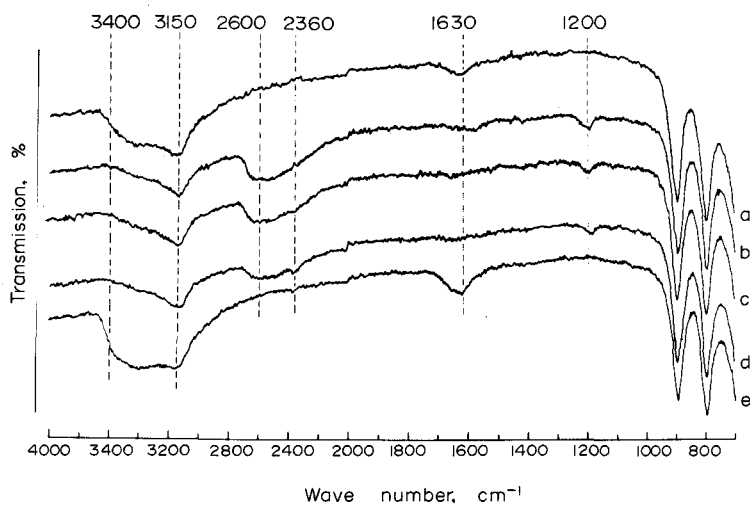

Fig. 3. Effect of D$_2$O exposure on the i.r. spectra of synthetic goethite, (a) before D$_2$O exposure, (b) after 89 hr over D$_2$O, (c) after 4 hr evacuation following (b), (d) after 16 hr in 110°C oven following (c) and (e) after 98 hr over H$_2$O at room temperature following (d).
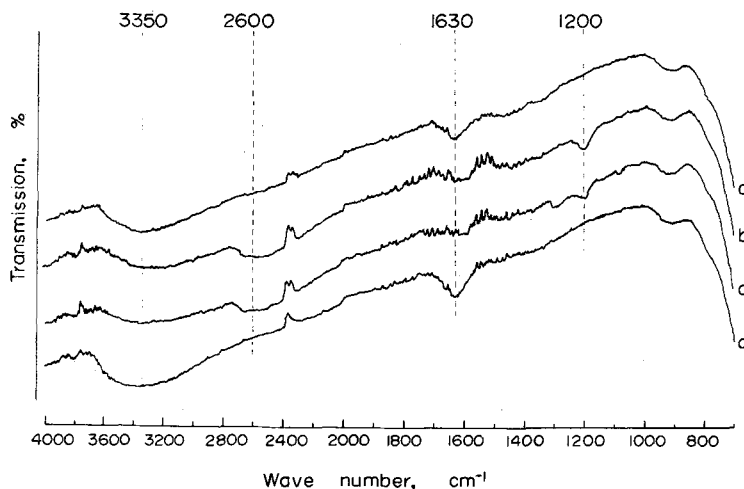
Fig. 4. Effect of D_2O exposure on the i.r. spectra of amorphous hydrated ferric oxide, (a) before D_2O exposure, (b) after 87 hr over D_2O, (c) after 1 hr evacuation following (b), and (d) after 90 hr over H_2O at room atmosphere following (c).

We could find no i.r. evidence in the literature indicating the temperature required to remove the last traces of residual water from goethite, or the nature of the goethite surface on removal of this water; i.e. evidence as to whether the goethite surface terminates in chemisorbed hydroxyl as does hematite and anatase. However, Jurinak (1964) has determined the change in water adsorption on hematite, anatase and goethite with increasing preheat or activation temperature under high vacuum. He found water adsorption to increase up to activation temperatures of 425, 280 and 195°C for hematite, anatase and goethite, respectively. However, X-ray analysis showed definite evidence for the presence of hematite in the goethite sample heated to 195°C; presumably, hematite was not present at 150°C. The water adsorbed on the goethite sample with 150°C activation was about 0·6 of a monolayer, compared to the monolayer coverage measured by nitrogen adsorption. Probably, additional water was adsorbed on the samples activated above 150°C, which suggests that the i.r. spectra of goethite in Fig. 2, evacuated at room temperature, reflect approximately a monolayer of water. This conclusion is only tentative, however, since the temperature required to remove the last traces of adsorbed water may also result in conversion of goethite to hematite. Further, the activation process may result in removal of chemisorbed hydroxyl as well as residual water, as in the case of hematite.

Adsorption–desorption isotherms and surface areas

Water vapor adsorption and desorption isotherms, with relative pressure as the independent variable, for

goethite and amorphous hydrated ferric oxide at 25°C are shown in Fig. 5. Similar isotherms at 15 and 35°C were essentially the same and are not shown. This is
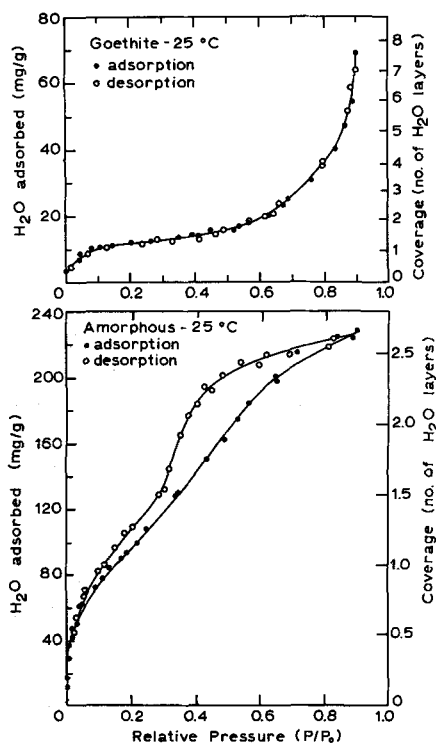

Fig. 5. Water vapor adsorption–desorption isotherms (relative pressure) at 25°C on goethite and amorphous hydrated ferric oxide outgassed at room temperature.
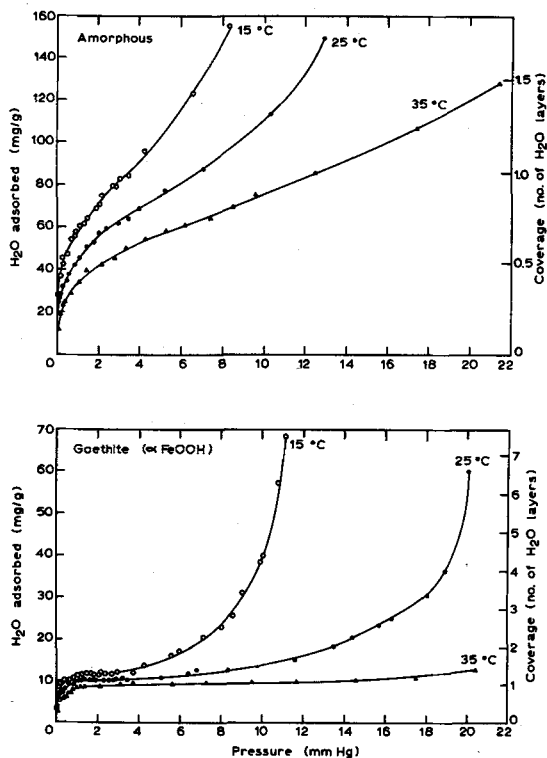
Fig. 6. Adsorption of water vapor on goethite and amorphous hydrated ferric oxide outgassed at room temperature.

further evidence that the adsorbing surfaces were stable during the period of study. The amorphous material adsorbed approximately three times more water than goethite and showed a significant hysteresis effect. In contrast, goethite showed no detectable hysteresis. The hysteresis displayed by the amorphous material is probably due to capillary condensation, since electron micrographs show the sample to consist of large aggregates compared to the discrete goethite particles (Landa and Gast, 1973). Surface areas of goethite and the amorphous material, calculated by BET theory from the 25°C adsorption data, are 32 and $320 \, m^2 \, g^{-1}$ respectively, corresponding to monolayers of 9·1 and 85·9 mg of water g^{-1} of sample. The latter value is the same as that found for synthetic goethite by Hingston, Posner and Quirk (1968). In comparison, Jurinak (1964) reported surface areas of about $16·4 \, m^2$ g^{-1} for a commercial source of goethite for both nitrogen and water vapor adsorption.

Experimental entropies of adsorption

Water vapor adsorption isotherms, with pressure as the independent variable, at 15, 25 and 35°C for goethite and amorphous hydrated ferric oxide are shown in

Fig. 6. Spreading pressures, ϕ, evaluated from these results according to equation (3) are shown in Fig. 7 as functions of water vapor pressure in mm Hg. The integral entropies of adsorption. ΔS(ads.) were in turn evaluated at 25°C from the slope of $\ln p$ vs T plots at constant spreading pressure according to equation (1). The results are shown in Fig. 8 as functions of fractional coverage of the surface.

As indicated earlier, the initial degassed goethite surface was covered by approximately one layer of physically adsorbed water, very strongly hydrogen bonded to the surface at least in part through the structural hydroxyls (Jurinak, 1971). Therefore, the first water adsorbed in this study is actually the second layer of physically adsorbed water on the goethite surface. In the case of the amorphous material, however, the observed adsorption apparently is the first physically adsorbed water layer, but the nature of the underlying surface is less well defined.

Values of ΔS(ads.) for mobile and immobile layers of adsorbed water, calculated by McCafferty and Zettlemoyer (1970) using statistical mechanical methods, are also indicated in Fig. 8 along with their experimental values for the first layer of water physically adsorbed on hematite. As in the case of hematite, the experimental values of ΔS(ads.) for goethite and the amorphous material generally agree more closely with the theoretical values for immobile rather than mobile layers. Thus, both the first physically adsorbed water layer on the amorphous material, and the second on goethite are localized through a hydrogen bonding mechanism. In the case of goethite, this hydrogen bonding would be between the first and second water layers, again reflecting the very strong hydrogen bonding between the first layer and the α-FeOOH surface. For the amorphous material, the nature of the hydrogen bonding between the first water layer and the surface is less well defined due to uncertainties in the nature of this surface after evacuation at room temperature.

The ΔS(ads.) values for goethite especially, and to a lesser extent for the amorphous material, are above those calculated for an immobile layer. Experimental uncertainties and small variations in the frequency of vibration used in calculating the entropy values for an immobile layer (McCafferty and Zettlemoyer, 1970), can probably account for these deviations in the case of the amorphous material. The larger deviation between the values for goethite and those calculated for the immobile layer may be associated with changes in the structure of the first as well as the second water layer. That is, the observed entropy values reflect any perturbations in the sorbent surface which occur during the adsorption process as well as entropy changes of the adsorbed water itself.
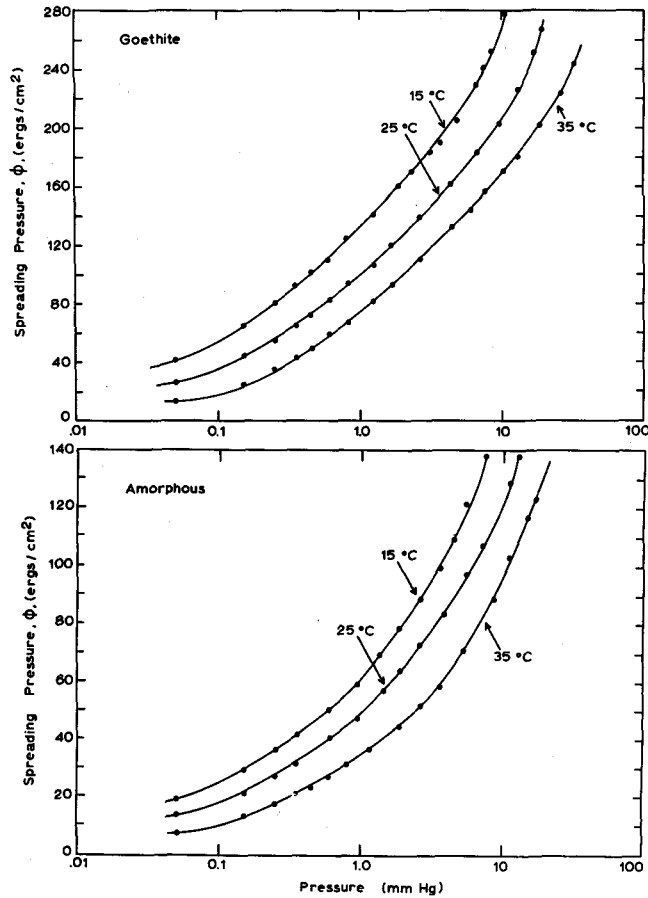
Fig. 7. Spreading pressure of water vapor on goethite and amorphous hydrated ferric oxide as a function of coverage.
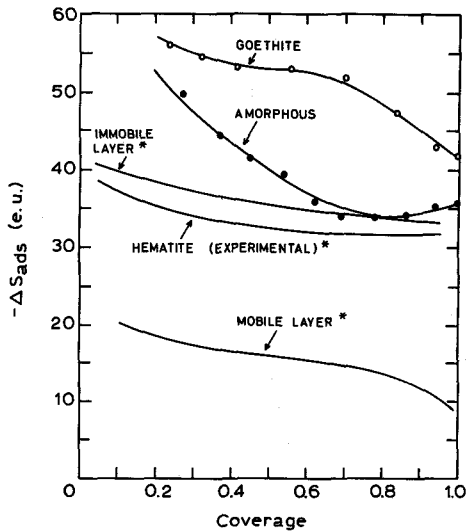

Fig. 8. Comparison of experimental entropies of adsorption at 25°C for goethite and amorphous hydrated ferric oxide with theoretical entropies for mobile and immobile absorbed films and experimental values for hematite reported by McCafferty and Zettlemoyer (1970).

SUMMARY AND CONCLUSIONS

I.R. absorption spectra of amorphous hydrated ferric oxide show the surface to be free of sorbed water after extended evacuation at 25°C. However, due to the diffuse nature of the spectra, it is not possible to tell whether the evacuated surface terminates in a chemisorbed hydroxyl layer as does hematite and anatase. In contrast, significant quantities of residual water remain on the goethite surface after extended evacuation at 25°C, indicating that the first layer of adsorbed water is hydrogen bonded more strongly to the surface than in the case of either hematite or the amorphous material.

Experimental integral entropy values for the first physically adsorbed water layer on the amorphous material and the second layer on goethite were greater than those previously reported for hematite, reflecting strong hydrogen bonding and in turn increased acidity of the adsorbed water. However, a greater total surface activity would be expected for the amorphous material than for goethite due to the greater surface area; i.e.

320 m^2 g^{-1} for the amorphous material vs 32 m^2 g^{-1} for goethite.

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Résumé—On a étudié par absorption infrarouge et mesure de l'adsorption de la vapeur d'eau, l'interaction entre l'eau et les surfaces d'une goethite de synthèse (α-Fe OOH) et d'oxyde ferrique hydraté amorphe. Les résultats de l'infrarouge montrent que les dernières traces d'eau adsorbée physiquement sont chassées du matériau amorphe par dégazage à 25°C. Par contre, la goethite retient environ une monocouche d'eau adsorbée physiquement lors du même dégazage. Cette monocouche d'eau présente sur la goethite est probablement liée par pont hydrogène au moins en partie avec les hydroxyles de constitution; elle est facilement échangeable avec D$_2$O.

Les entropies intégrales d'adsorption ont été évaluées à partir des isothermes d'adsorption de vapeur d'eau à 15, 25 et 35°C, et comparées aux valeurs pour les couches mobiles et immobiles calculées en appliquant la mécanique statistique (McCafferty et Zettlemoyer, 1970). Les valeurs de l'entropie pour la première monocouche d'eau adsorbée physiquement sur la matériau amorphe et la seconde monocouche sur la goethite, sont à peu près égales ou supérieures à celles qui sont calculées pour une couche immobile, ce qui indique de fortes liaisons hydrogène entre l'eau et chacune des surfaces. L'écart plus grand qui existe entre les valeurs de l'entropie pour la goethite et celles qui sont calculées pour une couche immobile peut être associé aux changements de structure aussi bien de la première que de la seconde couche d'eau adsorbée physiquement. Les aires des surfaces, calculées selon la méthode BET sont respectivement de 320 et 32 m^2 par gramme pour le matériau amorphe et la goethite. Comme l'activité de la surface unitaire est probablement du même ordre de grandeur pour les deux matériaux, il en découle que lorsque le matériau amorphe cristallise pour former la goethite, il y aurait une réduction de l'activité de la surface totale proportionnellement à la réduction de l'aire de la surface.

Kurzreferat—Die Wechselwirkung von Wasser mit synthetisch hergestelltem Goethit (α-FeOOH) und amorphen hydratisierten Fe^{III}-oxidoberflächen wurde mittels Messung der Infrarotabsorption und der Wasserdampfadsorption untersucht. Die Infrarotergebnisse zeigen, daß die letzten Spuren von physikalisch adsorbiertem Wasser von dem amorphen Material durch Entgasen bei 25°C entfernt werden. Im Gegensatz hierzu hält bei ähnlichem Entgasen Goethit annähernd eine Einzelschicht physikalisch adsorbierten Wassers zurück. Diese Wasserschicht an Goethit, die vermutlich wenigstens teilweise mit Gitterhydroxylionen durch Wasserstoffbrücken verbunden ist, kann leicht mit D$_2$O ausgetauscht werden.

Die integralen Adsorptionsentropien wurden aus den Wasserdampfadsorptionsisothermen bei 15, 25 und 35°C berechnet und mit den Werten für bewegliche und unbewegliche Schichten durch Anwendung der statistischen Mechanik verglichen (McCafferty and Zettlemoyer, 1970).

Sowohl für die erste physikalisch adsorbierte Einzelschicht des Wassers an dem amorphen Material als auch für die zweite Einzelschicht an Goethit waren die Entropiewerte etwa dieselben oder größer

als die für eine immobile Schicht berechneten. Dies deutet auf eine starke Wasserstoffbrückenbindung des Wassers an beiden Oberflächen hin. Die größere Abweichung zwischen den Entropiewerten für Goethit und den für unbewegliche Schichten berechneten Werten mag mit Veränderungen in der Struktur sowohl der ersten als auch der zweiten physikalisch adsorbierten Wasserschicht zusammenhängen. Die unter Verwendung der BET-Methode berechneten Oberflächen betrugen 320 m^2 für das amorphe Material und 32 m^2/g für Goethit. Da die spezifische Oberflächenaktivität wahrscheinlich für beide Stoffe dieselbe ist, würde sich eine der Verminderung der Oberfläche proportionale Verminderung der gesamten Oberflächenaktivität ergeben.

Резюме — ИК-спектрами поглощения и измерением адсорбции водяного пара изучалось взаимодействие с водой синтетического гетита (α-FeOOH) и аморфных гидратных поверхностей окиси железа. ИК-результаты показали, что последние следы физически адсорбированной воды удаляются с аморфного материала дегазированием при температуре 25°C, и наоборот при подобном дегазировании гетит сохраняет приблизительно молекулярный слой по крайней мере, частично связан водородом со структурными гидроксилами легко обменим с D$_2$O.

Интегральные энтропии адсорбции оценивались по изотермам адсорбции водяного пара при 15, 25 и 35°C и сравнивались со значениями для мобильных и немобильных слоев, рассчитанных статистическо-механически (МкКафферти и Зеттлемойер, 1970). Энтропийные значения для первого физически адсорбированного молекулярного слоя воды на аморфном материале, так и для второго молекулярного слоя на гетите были почти что одинаковыми или более, чем вычисленные для немобильного слоя, указывая на сильную водородную связь воды обеих поверхностей. Большое расхождение между энтропийными значениями гетита и значениями, высчитанными для немобильного слоя может быть связано с изменениями структуры как первого, так и второго физически адсорбированных слоев воды. Площади поверхности, рассчитанные по методу ВЕТ, были 320 и 32 м^2/г для аморфного материала и гетита, соответственно. Так как активность единицы поверхности, повидимому, идентична для обоих материалов, выходит, что по мере того как аморфный материал кристаллизируется в гетит, происходит общее уменьшение активности поверхности пропорциональное уменьшению ее площади.