The Intrinsic Equilibrium Constants of the Surface Hydroxyl Groups of Maghemite and Hematite

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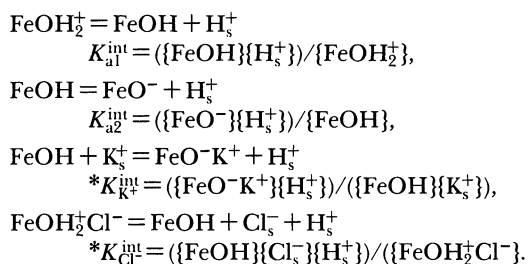
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The intrinsic equilibrium constants of the surface hydroxyl groups, which describe the ionization of surface hydroxyl groups and the complexation of ions of a KCl electrolyte, were calculated with the surface charge densities determined by the potentiometric titration, and with the surface site densities evaluated by the surface hydroxyl group densities. The values of the intrinsic ionization constants, K_{a1}^{int} and K_{a2}^{int} of maghemite, are higher than those of hematite, and the differences of these values have a tendency for $\Delta pK_{a1}^{int} < \Delta pK_{a2}^{int}$. The values of the intrinsic complexation constants, $*K_{K^+}^{int}$ and $*K_{Cl^-}^{int}$, of maghemite are higher than those of hematite. These results could be attributed to the differences of the electron densities of the oxygen atoms of the surface hydroxyl groups, which are linked to those in the bulk those of maghemite are lower than those of hematite. Also, the differences become smaller with increasing number of bonding protons.

Maghemite is widely used as a magnetic material for magnetic recording tapes and, hence, information concerning the surface properties of maghemite is essential for controlling the manufacturing conditions. Our previous papers[1,2] looked at the PZC (Point of Zero Charge) and the heat of immersion in water of maghemite, and clarified that the difference in the characteristics of the surface hydroxyl groups for maghemite and hematite arose from differences in the crystal structure. However, little work has been reported on the surface properties of maghemite, and no work has been reported concerning the intrinsic equilibrium constants of the surface; there have, however, been some reports on hematite.[3]

In the present work the intrinsic equilibrium constants of the surface hydroxyl groups, which describe the ionization of the surface hydroxyl groups and the complexation of K^+ and Cl^- ions with the oxide surface, were calculated using the surface charge densities determined by potentiometric titration, and with the surface site densities evaluated using the surface hydroxyl group densities.

In the site-binding theory of the electrical double layer on oxides proposed by Yates et al.[4] and extended by Davis et al.[5] and James et al.,[3,6] the following reactions occur at the iron oxide surface and are described by their equilibrium constants:

$FeOH_2^+ = FeOH + H_s^+$
$\quad K_{a1}^{int} = (\{FeOH\}\{H_s^+\})/\{FeOH_2^+\}$,

$FeOH = FeO^- + H_s^+$
$\quad K_{a2}^{int} = (\{FeO^-\}\{H_s^+\})/\{FeOH\}$,

$FeOH + K_s^+ = FeO^-K^+ + H_s^+$
$\quad *K_{K^+}^{int} = (\{FeO^-K^+\}\{H_s^+\})/(\{FeOH\}\{K_s^+\})$,

$FeOH_2^+Cl^- = FeOH + Cl_s^- + H_s^+$
$\quad *K_{Cl^-}^{int} = (\{FeOH\}\{Cl_s^-\}\{H_s^+\})/(\{FeOH_2^+Cl^-\})$.

Here, subscript s denotes the surface; $\{H_s^+\}$, $\{K_s^+\}$ and $\{Cl_s^-\}$ are the ionic concentrations at the surface, and are related to the bulk solution concentrations $\{H^+\}$, $\{K^+\}$ and $\{Cl^-\}$ by Boltzmann's distribution as follows:

$\{H_s^+\} = \{H^+\} \exp (-F\psi_o/RT)$,

$\{K_s^+\} = \{K^+\} \exp (-F\psi_d/RT)$,

and

$\{Cl_s^-\} = \{Cl^-\} \exp (-F\psi_d/RT)$,

where F, ψ_o, and ψ_d denote Faradays constant, the potential at the surface, and the potential at the plane of "ion pair" formation, respectively.

For the determination of K_{a1}^{int}, K_{a2}^{int}, $*K_{K^+}^{int}$ and $*K_{Cl^-}^{int}$, James et al.[3,6] have proposed a "double extrapolation technique," which is an excellent method for this purpose and was applied in the present work. There is, however, one significant problem regarding how to determine the value of the surface site density, which affects the final values of the above-mentioned constants. Regarding hematite, the value for the site density varies over the range from 3.1 to 22.4 sites nm^{-2}.[3] In the present work, the measured surface hydroxyl group densities were used as the surface site densities.

Experimental

Materials. The maghemite sample used in the present work was prepared from acicular synthetic α-FeOOH (geothite) by sequential dehydration, reduction and oxidation processes. The hematite sample was prepared by a heat treatment of the above-mentioned maghemite sample in air at 550 °C. In all cases the samples were purified as follows. They were first washed with an alkali solution, then with distilled water, and finally by electrodialysis. The samples and purification procedure are the same as those reported previously.[1] The specific surface area of the samples were 18.6 m^2g^{-1} for maghemite and 16.0 m^2g^{-1} for hematite by the BET method of nitrogen adsorption at liquid-nitrogen temperature; the cross-sectional area of the nitrogen molecule was assumed to be 16.2 $Å^2$.

Potentiometric Titration Method. Two grams of sample were dispersed into 50 ml of aqueous solution and adjusted to a certain value of ionic strength by the addition of KCl. The titrant cell was a 100 ml polyethelene cup with a tightly sealed cap (having stirring Teflon blades) inserted into the center of the cell. A combination electrode comprising glass and calomel electrodes (Mettler DG-111), a thermome-

ter, a microburet and an inlet and outlet for purified nitrogen gas of saturated water vapor were also inserted into the cell through the cap.[7] The titrant cell was positioned in a water bath, in which thermostatted water was circulated so as to maintain a constant cell temperature of 25 °C. The amount of titrant added and the pH of the suspension were controlled and recorded by an auto titrator (Mettller DL-40RC Memo Titrator). Titration was performed with a 0.1 M (1 M=1 mol dm^{-3}) HCl or KOH standard solution. Then, 0.05 ml of the titrant was added at 3-min intervals. Blank titration was performed in the same manner as that described above, except for the existence of the samples.

XPS Measurements. Maghemite and hematite samples were first pelletized, and then sputtered with Au and used for the measurement by ESCA 750 (Shimadzu Seisakusho Co., Ltd.). The chemical shifts of the binding energy of O(1s) of both samples were determined with a reference peak of Au(4f).

Results and Discussion

Surface Site Densities and Surface Charge Densities. For the determination of the constants (K_{a1}^{int}, K_{a2}^{int}, $*K_{K+}^{int}$, and $*K_{Cl-}^{int}$) using the double-extrapolation method, the fractional ionization, $\alpha_{\pm}$ (expressed as follows) is very important and changes the final value of these constants:

$$\alpha_{\pm} = \sigma_0/FN_s,$$

where σ_0 is the surface charge density and N_s is the surface site density (expressed as follows) and corresponds to the surface hydroxyl group density:

$$N_s = \{FeOH_2^+\} + \{FeOH_2^+Cl^-\} + \{FeOH\} + \{FeO^-\} + \{FeO^-K^+\}.$$

Though the value of σ_0 can be determined by potentiometric titration, N_s has various values which depend on the determination methods or estimation assumptions.[3] In the present work the most appropriate values for N_s, determined according to the amounts of chemisorbed water, were applied.

For the evaluation and examination of the values of N_s applied in the present work, the numerical parameters determined in a previous study[2] were used (listed in Table 1). V_p is the amount of water per unit area in a physisorbed monolayer (determined by the BET method of water adsorption), V_c is the number of the hydroxyl groups per unit area, and $S_{Fe^{3+}}$ is the average number of the surface iron ions per unit area (derived from the X-ray density of D_x of the crystal[8]).

Morimoto et al.[9] proposed a hydrated iron oxide

surface model which included the surface ions, as well as the chemisorbed and physisorbed water. Two surface iron ions share one molecule of chemisorbed water; these two neighboring hydroxyl groups are connected through hydrogen bonds to one physisorbed water of the first layer.

This model has been verified by the numerical correspondence between the surface densities of iron ions as well as both chemisorbed and physisorbed water. There is also the fact that the ratio between the surface density of iron ions ($S_{Fe^{3+}}$) and the surface hydroxyl group density of chemisorbed water (V_c) is 1 : 1 and the ratio between the physisorbed water density (V_p) and the surface hydroxyl group density (V_c) is 1 : 2. These numerical correspondences have been found to be reasonable regarding the present samples (Table 1): $S_{Fe^{3+}} \approx V_c$ and $V_p/V_c \approx 0.5$. These results strongly support the validity of the values of V_c, and of its application as N_s.

The surface charge densities of the σ_0 values of the maghemite and hematite samples determined by potentiometric titration are shown in Figs. 1 and 2, respectively. The plotted values were extracted from the titration curves (described in the experimental section) at the pH of the plotted points.
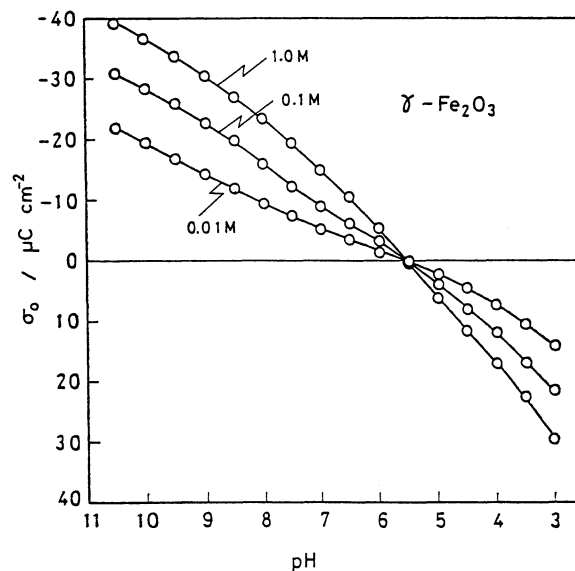

Fig. 1. The surface charge density of maghemite (γ-Fe$_2$O$_3$) in aqueous dispersion as functions of KCl electrolyte concentration and pH at 25 °C.

Table 1. Numerical Parameters of the Surfaces of Maghemite (γ-Fe$_2$O$_3$) and Hematite (α-Fe$_2$O$_3$)

	S_N[a]	V_p[b]	V_c[c]	V_p/V_c	D_x[d]	$S_{Fe^{3+}}$[e]
	m^{2}g^{-1}	H$_2$O's nm^{-2}	OH's nm^{-2}		g cm^{-3}	ions nm^{-2}
Maghemite	18.6	5.52	11.8	0.47	4.907	11.1
Hematite	16.0	5.85	12.8	0.46	5.277	11.7

a) Specific surface area determined by the BET method with N$_2$. b) Surface density of physisorbed water of the first monolayer. c) Surface density of the surface hydroxyl groups. d) X-ray density of crystal.[8] e) Surface density of the Fe^{3+} ions calculated by D_x.
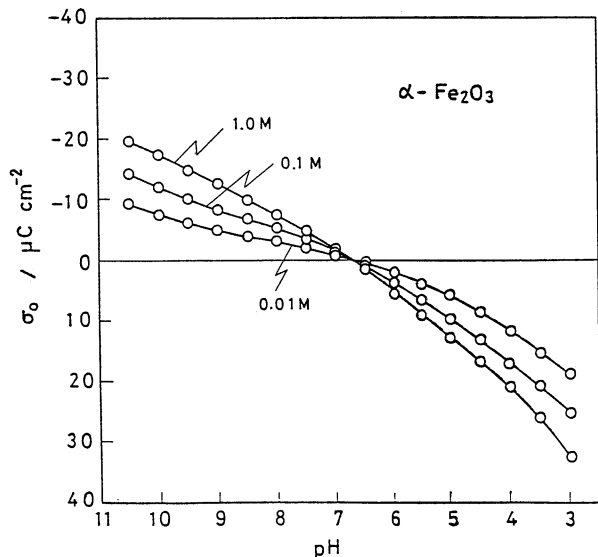
Fig. 2. The surface charge density of hematite (α-Fe_2O_3) in aqueous dispersion as functions of KCl electrolyte concentration and pH at 25 °C.

Determination of the Equilibrium Constants. The intrinsic ionization constants of the surface hydroxyl groups (K_{a1}^{int} and K_{a2}^{int}) can be written as

$$pK_{a1}^{int} = pH + \log\{\alpha_+/(1-\alpha_+)\} + (F\psi_o/2.3\ RT)$$
$$= pQ_{a1} + (F\psi_o/2.3\ RT),$$

and

$$pK_{a2}^{int} = pH - \log\{\alpha_-/(1-\alpha_-)\} + (F\psi_o/2.3\ RT)$$
$$= pQ_{a2} + (F\psi_o/2.3\ RT),$$

since the value of the potential at the surface is unknown throughout the pH range (with the exception of the PZC, at which ψ_o is equal to zero). K_{a1}^{int} and K_{a2}^{int} cannot be obtained directly from the above formulas. The double-extrapolation plots[3,6] are applied to obtain K_{a1}^{int} and K_{a2}^{int}. With this method, the surface acidity quotient, $pQ_a=pH\pm\log\{\alpha_\pm/(1-\alpha_\pm)\}$, was determined for each experimental titration data point and for ranging the ionic strength (plotted as a function of $10\alpha_\pm + C_{KCl}^{1/2}$). Plots of maghemite and hematite are shown in Figs. 3 and 4, respectively. For each ionic strength, curves were extrapolated through the points to the condition where $\alpha_\pm=0$. The extrapolated points are shown as solid squares. These extrapolation points, themselves, are extrapolated to zero supporting electrolyte concentration: that is, $\alpha_\pm=0$ and $C_{KCl}=0$. In addition, other curves can be extrapolated for conditions of constant surface charge, i.e. $\alpha_\pm=$const., to a zero supporting electrolyte concentration of $C_{KCl}=0$. These extrapolated points for constant $\alpha_\pm$ are shown as open squares, and form a curve for double extrapolation: that is, $C_{KCl}=0$, extrapolated to $\alpha_\pm=0$.

The intrinsic ionization constants of pK_{a1}^{int} and pK_{a2}^{int} obtained by these plots are 2.7±0.3 and 8.3±0.3 for maghemite, and, 3.2±0.3 and 10.2±0.3 for hematite,
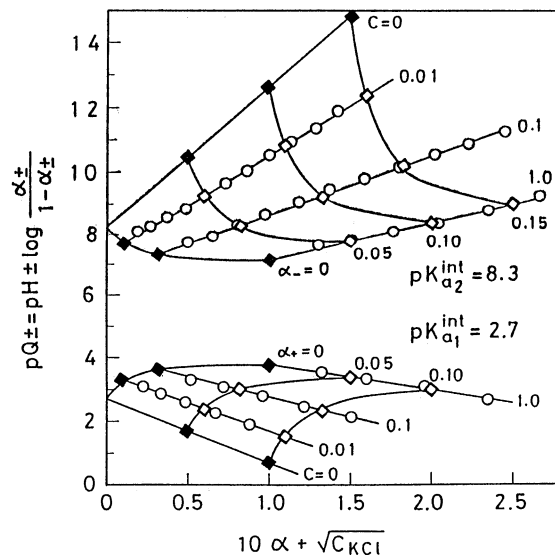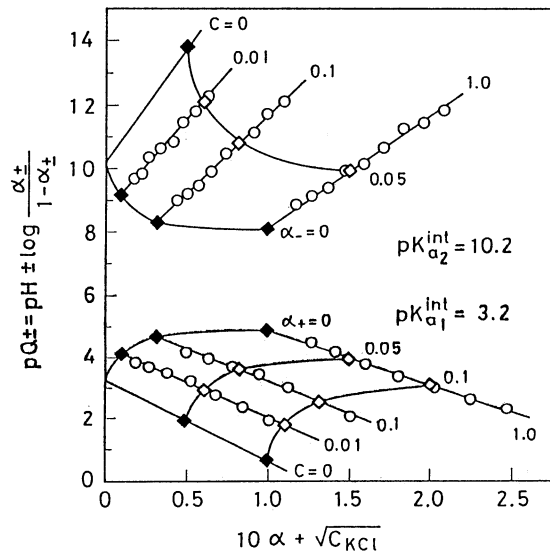

Fig. 3. Double extrapolation plot for determination of pK_{a1}^{int} and pK_{a2}^{int} showing the variation of surface acidity quotients, pQ_a, for dissociation of positive and negative sites on maghemite (γ-Fe_2O_3) in aqueous dispersion at 25 °C, with fractional ionization and KCl electrolyte concentration.

Fig. 4. Double extrapolation plot for determination of pK_{a1}^{int} and pK_{a2}^{int} showing the variation of surface acidity quotients, pQ_a, for dissociation of positive and negative sites on hematite (α-Fe_2O_3) in aqueous dispersion at 25 °C, with fractional ionization and KCl electrolyte concentration.

respectively. The intrinsic ionization constants of K_{a1}^{int} and K_{a2}^{int} are related to the value of the PZC (via the following equation), since at the PZC, $\{FeO^-\}_{PZC}=\{FeOH_2^+\}_{PZC}$ and $\{H_s^+\}_{PZC}=\{H^+\}_{PZC}$ ($\psi_o=0$):

$$pH_{PZC} = 1/2\ (pK_{a1}^{int} + pK_{a2}^{int}).$$

This relationship can be pertinent to both maghemite and hematite, referring to the values of pH_{PZC} of 5.5 for maghemite and 6.7 for hematite[1] (Table 2). For

Table 2.   Surface Ionization and Complexation Constants
for Maghemite (γ-Fe$_2$O$_3$) and Hematite (α-Fe$_2$O$_3$)

	pK_{a1}^{int}	pK_{a2}^{int}	$(pK_{a1}^{int}+pK_{a2}^{int})/2$	$pH_{PZC}^{1)}$	$p^*K_{K^+}^{int}$	$p^*K_{Cl^-}^{int}$
Maghemite	2.7±0.3	8.3±0.3	5.5±0.3	5.5	7.1±0.3	3.8±0.3
Hematite	3.2±0.3	10.2±0.3	6.7±0.3	6.7	8.1±0.3	4.9±0.3
$-\Delta pK$ (average)	0.5	1.9	1.2	1.2	1.0	1.1

the value of the PZC of maghemite, an identical value of 5.5 was also confirmed by potentiometric titration with a commercially available maghemite sample having an acicular shape with a length of 0.2—0.4 μm and an acicular ratio of 8—10. The saturation magnetization is 73.0 emu g^{-1} and the specific surface area is 23.8 m^{2}g^{-1}. The purification of this sample was the same as that mentioned in the experimental section. For hematite, many titration measurements have been reported; those values of PZC which are more than 8, are 8.4,[10,11] 8.5,[12-14] and 8.4—9.3.[15] The reason for the higher values (compared to the present value of 6.7) could be attributed to the degree of hydration of the samples. All of the above-mentioned samples were prepared and measured in an aqueous systems without any unhydration process. Hematite prepared in an aqueous system has a hydrated layer at the surface,[10,11] and shows a very high surface density of the chemisorbed water;[13,14,16] the hydroxyl groups thus behave as surface sites, and also show a high IEP value[17,18] (Isoelectric Point). The values of pK_{a1}^{int} and pK_{a2}^{int} determined by titration data for the above samples, are $pK_{a1}^{int}=6.7\pm0.3$ and $pK_{a2}^{int}=10.3\pm0.3$,[3] with an apprehension for the underestimation of the surface site density of N_s. These values almost coincide with the values of pK's concerning Fe(OH)$_3$ (described below[19]). The contribution of the hydroxyl groups bonded directly to the crystal of hematite is considered to be small compared to those of hydrated iron(III) oxides:

$$Fe(OH)_2^+ + H_2O = Fe(OH)_3 + H^+ \quad pK_1 = 6.0\pm0.2$$
$$Fe(OH)_3 + H_2O = Fe(OH)_4^- + H^+ \quad pK_2 = 10.0\pm0.2$$
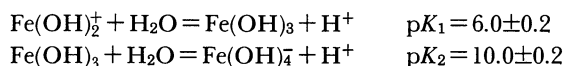
The values found in the present work are considered to be those of surface hydroxyl groups bonding to the crystal surface, with regard to the reasonability of the surface densities of the hydroxyl groups and the clear differences of the values between hematite and maghemite.

The intrinsic ionization constants for both steps of maghemite are higher than those of hematite. It is reasonable to consider that the value of pH$_{PZC}$ for maghemite is lower than that for hematite. More noticeable, however, the average difference of pK_{a1}^{int} between maghemite and hematite, i.e. ΔpK_{a1}^{int}, is higher than that of pK_{a2}^{int}, i.e. ΔpK_{a2}^{int} (Table 2).

Determination of the Intrinsic Complexation Constants. The intrinsic complexation constants of surface hydroxyl groups $^*K_{K^+}^{int}$ and $^*K_{Cl^-}^{int}$ are defined using the following formulas:

$p^*K_{K^+}^{int}$
$$= pH - \log\{\alpha_-/(1-\alpha_-)\} + \log\{K^+\} + \{F(\psi_o-\psi_d)/2.3\,RT\}$$
$$= p^*Q_{K^+} + \{F(\psi_o-\psi_d)/2.3\,RT\},$$

and

$p^*K_{Cl^-}^{int}$
$$= pH + \log\{\alpha_+/(1-\alpha_+)\} - \log\{Cl^-\} + \{F(\psi_o-\psi_d)/2.3\,RT\}$$
$$= p^*Q_{Cl^-} + \{F(\psi_o-\psi_d)/2.3\,RT\}.$$

In order to obtain the values of $^*K_{Cl^-}^{int}$ and $^*K_{K^+}^{int}$ with the double-extrapolation method,[3,6] the surface complexation quotient, $p^*Q=pH\pm\log\{\alpha_\pm/(1-\alpha_\pm)\}\mp\log\{C_{KCl}\}$, was plotted as a function of $10\alpha_\pm+\log C_{KCl}$. These plots for maghemite and hematite are shown in Figs. 5 and 6, respectively. For each ionic strength, a smooth curve drawn through the experimental points was extrapolated to $(10\alpha+\log C)=\log C$. These extrapolated points are shown as solid squares. At these points α and σ_o must be zero. A smooth curve through these points can be extrapolated to $(10\alpha+\log C)=0$, where since $\alpha=0$, $\sigma_o=0$, and $\log C=0$, $C=1$. In addition, a smooth curve can be drawn through the points of arbitary values of α, shown as open squares, and extrapolated to $\log C=0$ for that α. A smooth curve joining these $\log C=0$ points (shown as solid squares) and the experimental points of its $C_{KCl}=1$ (having a good fit with the extrapolated points) can be extrapolated to $(10\alpha+\log C_{KCl})=0$, where since $\log C_{KCl}=0$, $C_{KCl}=1$ and $\alpha=0$, $\sigma_o=0$. The intrinsic
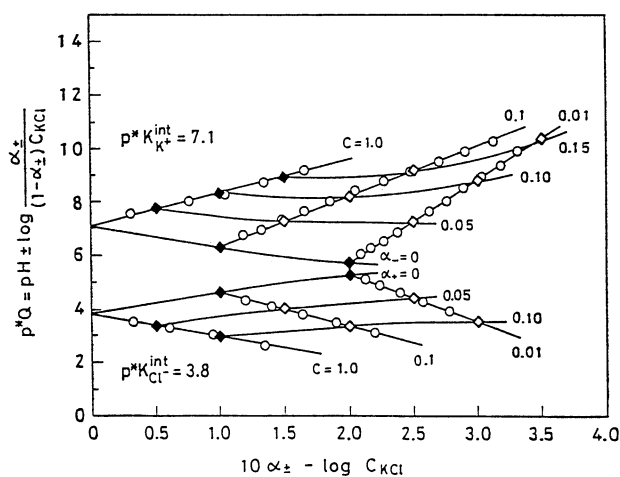

Fig. 5.   Double extrapolation plot for determination of $p^*K_{K^+}^{int}$ and $p^*K_{Cl^-}^{int}$ showing the variation of surface complexation quotients, p^*Q, for positive and negative sites on maghemite (γ-Fe$_2$O$_3$) in aqueous dispersion at 25 °C, with fractional ionization and KCl electrolyte concentration.
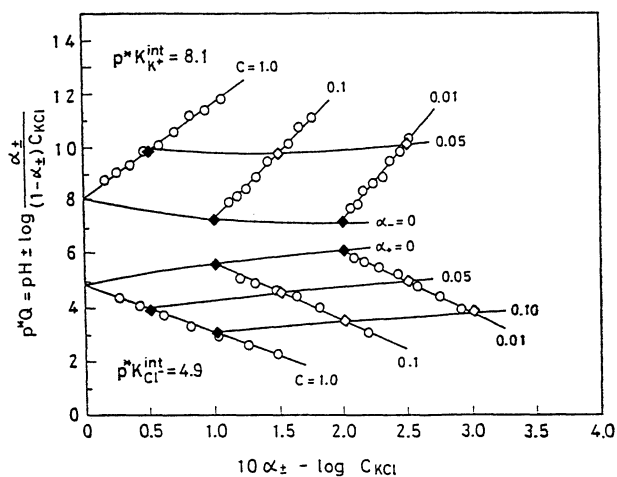
Fig. 6. Double extrapolation plot for determination of p*$K_{K^+}^{int}$ and p*$K_{Cl^-}^{int}$ showing the variation of surface complexation quotients, p*Q, for positive and negative sites on hematite (α-Fe$_2$O$_3$) in aqueous dispersion at 25 °C, with fractional ionization and KCl electrolyte concentration.

Fig. 7. The signal intensities of XPS of O(1s) for maghemite (γ-Fe$_2$O$_3$) as function of the binding energy.

Fig. 8. The signal intensities of XPS of O(1s) for hematite (α-Fe$_2$O$_3$) as function of the binding energy.

complexation constants of p*$K_{K^+}^{int}$ and p*$K_{Cl^-}^{int}$, obtained by two-extrapolation procedures, are 7.1±0.3 and 3.8±0.3 for maghemite, and 8.1±0.3 and 4.9±0.3 for hematite, respectively (Table 2). It can be found that the capability of the formation of the surface complexes of {FeO$^-$K$^+$} of maghemite is higher than that of hematite, and that the capability on {FeOH$_2^+$Cl$^-$} of maghemite is lower than that of hematite.

Dependence of Equilibrium Constants on Crystal Structure. These results show that the intrinsic ionization constants of K_{a1}^{int} and K_{a2}^{int} for maghemite are lower than those for hematite. These differences can be attributed to the different natures of the surface hydroxyl groups, which are strongly affected by the crystal structure of the bulk. The values of the intrinsic complexation constants of *$K_{K^+}^{int}$ and *$K_{Cl^-}^{int}$ for maghemite and hematite should be linked to the values of the intrinsic ionization constants of K_{a1}^{int} and K_{a2}^{int} for maghemite and hematite. Then, the results that the value of *$K_{K^+}^{int}$ for maghemite is higher than that for hematite, and the value of *$K_{Cl^-}^{int}$ for maghemite is lower than that for hematite, can be interpreted as follows: The higher value of *$K_{K^+}^{int}$ for maghemite implies that the formation of the surface complex of FeO$^-$K$^+$ is easier for maghemite than for hematite, and is considered to be due to the fact that the formation of the anionic surface site, FeO$^-$, is easier for maghemite than for hematite. The lower value of *$K_{Cl^-}^{int}$ for maghemite implies that the formation of a surface complex of FeOH$_2^+$Cl$^-$ is harder for maghemite than for hematite; this is considered to be due to the fact that the formation of a cationic surface site of FeOH$_2^+$ is harder for maghemite than for hematite.

The difference in nature of the surface hydroxyl groups due to the differences in the crystal structure must be examined by considering the nature of the
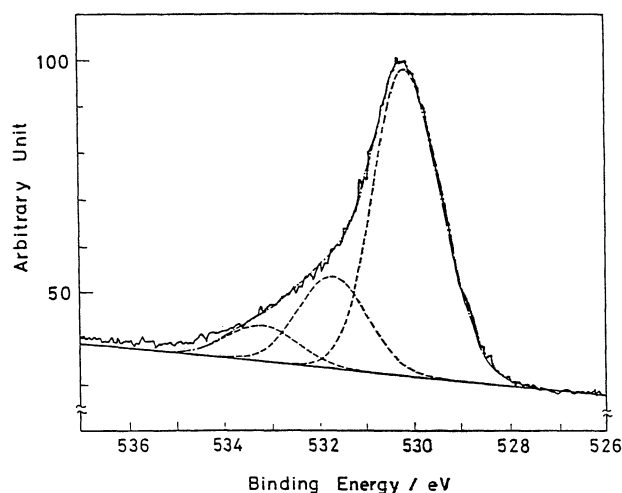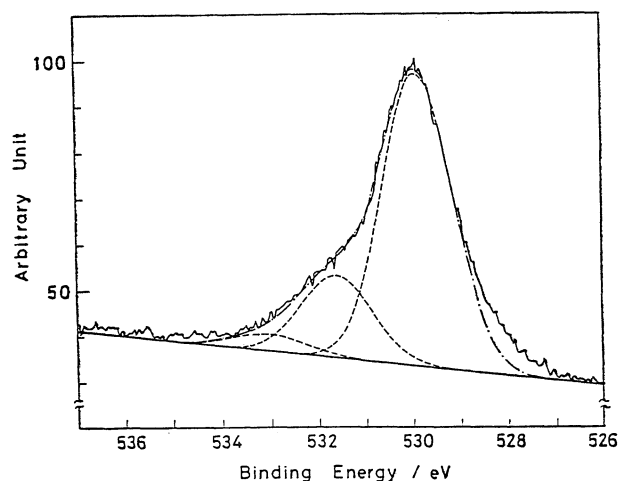
chemical bonds of Fe–O in the bulk of a crystal, which is considered to have an intimate correspondence with the chemical bonds of Fe–O (–H) of the surface hydroxyl groups. The above-mentioned fact that the crystal density (D_x) of maghemite is lower than that of hematite strongly suggests that the average bond length of Fe–O of maghemite is longer than that of hematite. The enthalpy of the crystal formation of maghemite is higher than that of hematite.[20] Then, the bond of Fe–O of maghemite is weaker and less polar than that of hematite, and the atoms in the crystal of maghemite are less ionic[21] than those of hematite; also, the electron density of the oxygen atoms in the crystal of maghemite is considered to be lower than that hematite. The electron density of the oxygen atoms can be examined by the XPS signal of the binding energy of O(1s) through its chemical shift. Figures 7 and 8 show the O(1s) spectra of both mag-

hemite and hematite, respectively. These spectra were observed to consist of the main strong peaks, attributed to the oxygen atoms of the crystal lattice, and to the additional low-intensity bands of high binding energies, with a curve fitting method. For the main peak of the oxygen atoms of the bulk, the higher binding energy of maghemite (530.1 eV), than that of hematite (529.9 eV), can be confirmed with a chemical shift of about 0.2 eV.[22] This result suggests that the electron desity of the oxygen atoms of the bulk of maghemite is lower than that of hematite. The electron density of the oxygen atoms of the surface hydroxyl groups is considered to be related to the electron density of the oxygen atoms of the bulk crystal. This consideration can be well supported by the fact that the additional bands, which are likely to be due to surface hydroxyl groups of maghemite, have higher binding energies than those of hematite, through inspections of the spectra in Figs. 7 and 8. The lower electron density of the oxygen atoms of the surface hydroxyl groups of maghemite, compared to that of hematite, could explain the origin of the lower values of pK_{a1}^{int} and pK_{a2}^{int} for maghemite than for hematite. It can also be discussed from the point of view of proton affinity, which decreases with the correspondence to the higher chemical shift of the binding energy of O(1s) of XPS.[23]

Concerning the differences of the values of pK_{a1}^{int} and pK_{a2}^{int} between maghemite and hematite, ΔpK_{a1}^{int} is higher than ΔpK_{a2}^{int}. The reason for these differences is considered to be due to the fact that the difference in the electron density of the oxygen atoms of surface hydroxyl groups between maghemite and hematite becomes smaller as the number of protons bonding to the oxygen atoms of the surface hydroxyl groups increases, such as $FeO^-<FeOH<FeOH_2^+$. Thus, the difference in the electron density of the oxygen atoms of the surface hydroxyl groups originating in the bulk crystal is decreased by bond formation of the oxygen atoms of the surface hydroxyl groups with protons.

Conclusion

1) The intrinsic ionization constants, K_{a1}^{int} and K_{a2}^{int}, of maghemite are higher than those of hematite. These facts can be attributed to a differences in the electron density of the oxygen atoms of the surface hydroxyl groups, which are, in turn, affected by the bulk crystal.

2) The differences in the values of K_{a1}^{int} and K_{a2}^{int} between maghemite and hematite have a tendency to be $\Delta pK_{a1}^{int}<\Delta pK_{a2}^{int}$. This tendency can be attributed to a decrease in the difference of the electron density of the oxygen atoms of the surface hydroxyl groups caused by an increase in the number of protons bonding to the oxygen atoms.

3) The intrinsic complexation constants, $*K_{K^+}^{int}$ and

$*K_{Cl^-}^{int}$, are higher than those of hematite. These differences in the intrinsic complexation constants arise from a differences in the intrinsic ionization constants.

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