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Dependence of the Heat of Immersion of Maghemite on the pH of an Aqueous Solution

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Synopsis. We examined the dependence on the pH value of the heat of immersion of maghemite in an aqueous system, and confirmed the peculiar finding that the pH value at the minimum heat occurs not at PZC, but at a higher pH. The reason for this is the existence of two types of surface hydroxyl groups (basic and acidic) which comprise all of the surface hydroxyl groups on maghemite. Moreover, the heat required for the adsorption of a proton on the surface hydroxyl group is higher than that for its desorption.

Maghemite is a ferrimagnetic inverse-spinel type iron oxide, and is widely used as magnetic pigments for magnetic recording media. The surface properties of maghemite pigments are very important for manufacturing this media. Previous studies[1—6] have clarified the surface properties of maghemite from the view-point of correlations with the bulk crystal structure.

The present report examines the pH dependence of the heat of immersion in water of maghemite, through which it is clarified that the pH value at minimum heat does not coincide with the pH value at PZC (Point of Zero Charge), but with a pH value higher than that at PZC. The above observation motivated the present investigations.

Experimental

Material. The maghemite sample of the present work was prepared from acicular synthetic goethite by sequential dehydration, reduction, and oxidation processes. Sample purification was performed as follows: washing with an alkali water solution, then distilled water and, finally, by electrodialysis.[1] The sample particles were observed, with a microscope, to have an acicular shape, and a specific surface area of 23.8 $m^2 g^{-1}$, determined by the BET method of nitrogen adsorption at liquid-nitrogen temperature, assuming the cross-sectional area of a nitrogen molecule to be 16.2 $Å^2$.

Heat of Immersion Measurements. A twin-type heat-conduction calorimeter (Tokyo Rikou MPC-2) was used, as reported previously.[2] The sample was degassed in a Pyrex glass ampoule at 25 °C for 8 h in a vacuum of 2×10^{-4} Pa before sealing. The measurements were carried out at 25.0 ± 0.1°C with a constant amount of the sample (0.80 g) and an aqueous solution (40.0 ml). The pH of this solution was adjusted with KOH and HCl; the ionic strength was adjusted to 0.01 M with KCl (1 M=1 mol dm^{-3}). Much attention was paid to the water content of the samples, since the heat was significantly affected by it. Four ampoules were prepared in one evacuation run; one of these was checked in a fixed condition, and the others were used for measurements in various pH systems. The heat for breaking of the ampoule was found to be 0.26 J, regardless of the pH of the aqueous solution.

Potentiometric Titration Method. Two grams of the sample were dispersed into 50 ml of an aqueous solution and adjusted to an ionic strength of 0.01 M by the addition of KCl. Titration was performed with HCl and KOH; the cell, apparatus, and methods which were used were reported previously.[3]

Results and Discussion

The value of PZC in the pH value was determined by a plot of the surface charge density versus the pH (Fig. 1), which was derived from the data of potentiometric titration. This plot indicates the PZC value of this maghemite sample is 5.5, which agrees with another reported value,[3] and supports high purity in the surface of the sample. The heats of immersion are plotted in Fig. 2 as a function of the pH value. Since the pH value changes during the measurement from the initial setting stage to the final immersion stage, the pH values of the final stage in equilibrium were used in the above-mentioned plots. The plots show that the minimum heat occurs at a pH of about 6.8. It would be reasonable to expect that the minimum heat occurred at PZC, where the heat accompanying the adsorption or desorption of protons to or from the surface hydroxyl groups should be lowest. In alumina systems, the pH values for the minimum heat and PZC are reported to be approximately equal.[7,8]

In the present study, we inquired into the nature of the surface hydroxyl groups of maghemite with the aim of understanding the reason for the discrepancy. As

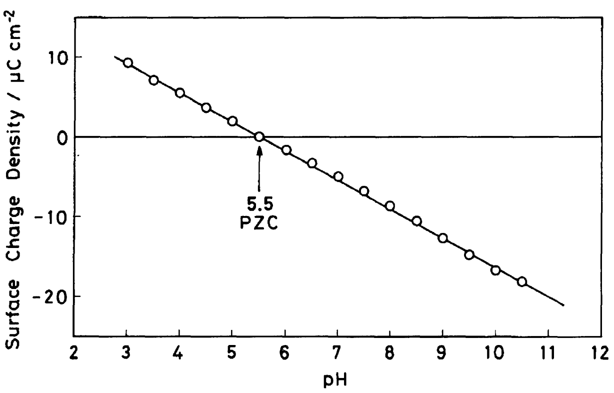

Fig. 1. Surface charge density of maghemite in an aqueous dispersion as a function of the pH at 25 °C.

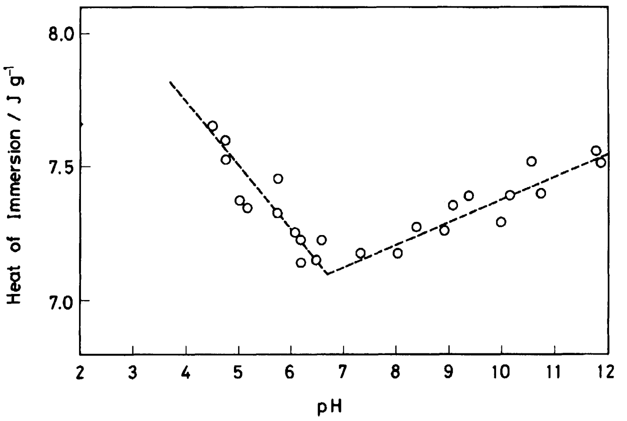

Fig. 2. Heat of immersion of maghemite in an aqueous system with an ionic strength of 0.01 M KCl, as a function of the pH at 25 °C.

has already been reported in previous studies,[4,5] the surface species on maghemite are classified into two typical kinds of surface hydroxyl groups, namely the acidic groups which bond to the surface iron ions at the tetrahedral sites, and the basic groups which bond to the same ions at the octahedral sites. We expect that the surface properties relating the surface to different hydroxyl groups, such as PZC or the heat of immersion, can be predicted by the addition of component values. In the case of PZC,[10,11] it has been verified that the additivity rule holds in maghemite.[2,3] In the present study, we applied the aforementioned hypothesis to the heat of immersion in an attempt to understand the discrepancy between the pH of the minimum heat and the PZC.

The linear relationship between the pH and the surface charge density (Fig. 1) implies an adsorption isotherm of the Frumkin-Temkin type; such an isotherm shows a linear relation between the coverage (θ) of the adsorbant and the logarithmic equilibrium concentration (C), namely $\theta = a \ln(bC)$. Here, a and b are constants. The differential heat (δh) of adsorption decreases linearly with the coverage by the means of an increase in the Coulombic repulsion in the process of the adsorption of protons or hydroxide ions, as follows:

$$\delta h = E_{\mathrm{m}} - (E_{\mathrm{m}} - E_{\mathrm{l}})\theta.$$

E_{m} is the maximum heat of adsorption, i.e. the heat of adsorption without electrostatic energy, and E_{l} is the minimum heat of adsorption at the final coverage stage. The integral heat (δH) of adsorption from $\theta = 0$ (at PZC) to θ increases parabolically with the coverage, as follows:

$$\delta H = \int_0^{\theta} \delta h \mathrm{d}\theta = E_{\mathrm{m}}\theta - 1/2(E_{\mathrm{m}} - E_{\mathrm{l}})\theta^2.$$

As mentioned above, the linear correlation is the result of adding the two linear correlations for the basic and acidic surface hydroxyl groups, with the componental weight ratio of the former to the latter groups being 5 : 3. PZC for the basic hydroxyl groups bonding to the surface iron ions in the octahedral sites is numerically calculated to be 6.7. This corresponds to the PZC of hematite, all surface hydroxyl groups of which are at the octahedral sites. A comparison with the measured[1] and estimated[1,2,4] values shows that the PZC values for the hydroxyl groups on maghemite bonding to the iron ions in the octahedral sites are reasonable. Moreover, the application of the additivity rule yields a PZC value of 3.5 for that at the tetrahedral sites.[10,11] These linear correlations are illustrated in Fig. 3.

The above-mentioned additivity rule may be applicable to the heat of immersion of maghemite. The differential heat of immersion of metal oxides with aqueous systems in the pH range higher than PZC is reported to be lower than that in the pH range lower than the PZC.[8] According to Blesa et al.,[9] the differential heat for the adsorption of protons is lower than that of hydroxyl ions; the heats of iron ions are 50 kJ mol⁻¹ for the former and 17 kJ mol⁻¹ for later. The heat profile versus the pH is diagrammed in Fig. 4 by calculations using the above-mentioned values and the coverage (θ)

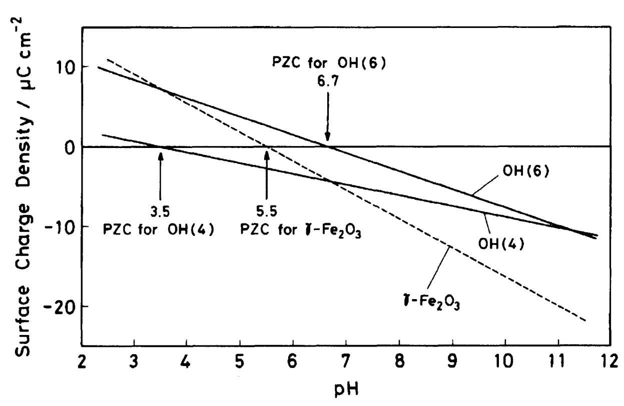

Fig. 3. Componental plots of the surface-charge density vs. the pH, for the basic and the acidic surface hydroxyl groups.

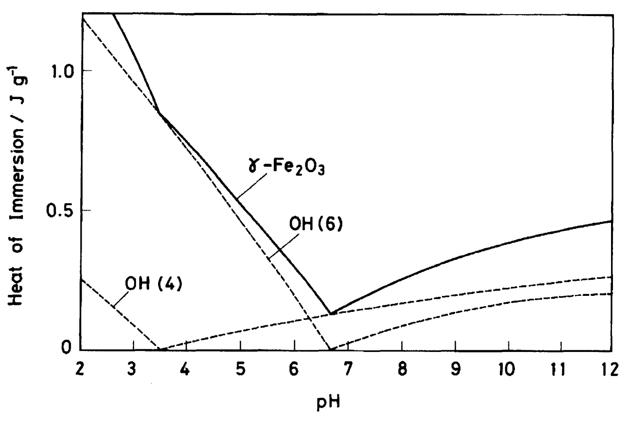

Fig. 4. Componental plots of the heat of immersion vs. the pH, for the basic and the acidic surface hydroxyl groups.

determined by the surface density of hydroxyl groups.[2] As is shown in Fig. 4, the value of the heat is a downward parabola with a large slope for a pH lower than PZC, and an upward parabola with a relatively small slope for a large value of the pH. The total heat profile of maghemite is obtained by the summation of the two profiles with different values of PZC. As is visualized in Fig. 4, the pH value of the minimum heat is almost the same as that of PZC of the basic surface hydroxyl groups, the value of which agrees with that estimated by the additivity rule mentioned above. The discrepancy between PZC and the pH of the minimum heat of immersion may be well explained by this mechanism.

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