On the Equi-adsorption Point of Hydrogen and Hydroxyl Ions at the Alumina-Water Interface

By

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The equi-adsorption point defined here as a pH value of the solution where hydrogen and hydroxyl ions are equal in adsorption density at oxide mineral-water interface is presented. The equi-adsorption point of alumina was found at pH 7.4 from the adsorption measurement, while the isoelectric point of the same material was at pH 9.0 in the electrophoresis study. It is shown that the equi-adsorption point is not always in agreement with the isoelectric point for oxide minerals. The equi-adsorption point of alumina is also determined to be at pH 7.5 by considering the equilibrium solubility diagram which is obtained from thermodynamical information for several reactions in the alumina-water system.

It is concluded that the adsorption of hydrogen and hydroxyl ions on oxide minerals is closely related to the chemical affinity between the constituent atoms of the mineral and the hydrogen or hydroxyl ion.

1. Introduction

As part of the fundamental study of the mechanism of the reaction between oxide mineral surface and collector ions in flotation, the authors have previously published several reports concerning the surface-chemical investigations on the adsorption of hydrogen and hydroxyl ions at the oxide-water interface[1~4]. A well-founded method for determining the adsorption density of hydrogen and hydroxyl ions on oxide was established to determine their adsorption isotherms. Furthermore, it was shown that the adsorption of hydrogen and hydroxyl ions at the oxide-water interface closely correlated with the heat of immersion in the oxide-water system and also with the pH value of an oxide particle suspension.

Once the adsorption isotherms of hydrogen and hydroxyl ions for a certain mineral have been determined, a pH value of water is obtained where hydrogen and hydroxyl ions are equal in adsorption density at the mineral-water inter-

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face. In the present paper the authors define this pH value as the equi-adsorption point of mineral. As previously reported, the equi-adsorption point of alumina correlates with the pH value of water where the heat of immersion in the alumina-water system is minimum and also with the buffered pH value of alumina particle suspension. Therefore, the equi-adsorption point of an oxide mineral is considered as one of the characteristic values in the surface-chemistry including the solid phase. The equi-adsorption point depending on the nature of mineral may play an important role in the collector-oxide mineral reaction.

In this paper the difference between the equi-adsorption point and the isoelectric point is shown by experiments using alumina, and then the relation between the equi-adsorption point and the chemical affinity of hydrogen and hydroxyl ions onto the mineral surface is also shown.

2. The Isoelectric Point and the Equi-adsorption Point

Many investigators have written about the isoelectric point of alumina; for example, P. G. Johansen[5] obtained 8.4 by means of the electrophoresis measurement, H. J. Modi et al[6] reported to be 9.45 by the streaming potential technique, and J. A. Yopps et al[7] and R. Fricke[8] showed that the isoelectric point of alumina ranged from pH 8.9 to 9.2.

As mentioned above, it is generally accepted that alumina is positively charged in neutral water, although investigators have given different values for the isoelectric point of alumina.

The authors used "Linde A" alumina which was provided by Union Carbide Corporation. Fig. 1 shows the pH dependence of ζ-potential for the alumina particles by the electrophoresis measurement using a Zeta meter.
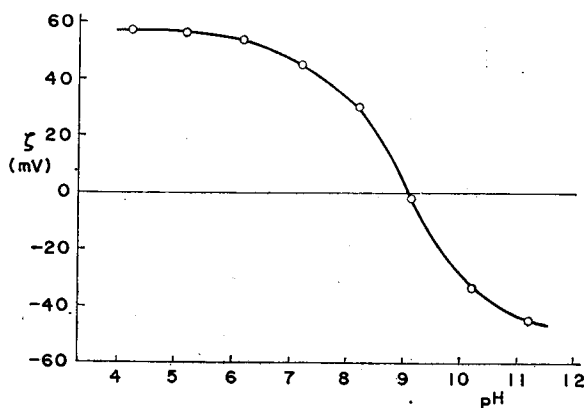

Fig. 1. ζ-potential of alumina as a function of pH.

As can be seen from Fig. 1, the alumina sample used in this experiment has its isoelectric point at pH 9.0. Therefore, the alumina particles are positively charged in water of the pH range less than the isoelectric point, whereas they are negatively charged in the alkaline solution more than pH 9.0.

G. A. Parks et al[9] assumed the isoelectric point as a pH value of solution where both hydrogen and hydroxyl ions adsorb equal amounts onto oxide surface, and thus on the basis of this assumption they attempted to determine the isotherms of hydrogen and hydroxyl ion adsorption. However, the assumption is not always true because solid particles are often inherently charged regardless of hydrogen and hydroxyl ion adsorption, and also because the slipping plane at which ζ-potential is induced may not agree with the boundary plane by which the adsorption layer for hydrogen and hydroxyl ions at the oxide-water interface is distinguished from the water bulk.
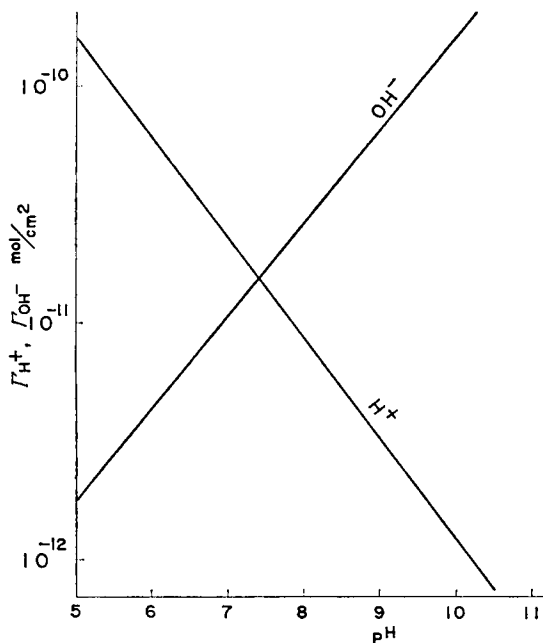

Fig. 2. Adsorption isotherms for hydrogen and hydroxyl ions.

Fig. 2 shows the adsorption isotherms of hydrogen and hydroxyl ions on the same material as used for Fig. 1. The method for determining the isotherms was described in detail in the previous paper[1]. Γ_{H^+} and Γ_{OH^-} represent the adsorption density of hydrogen and hydroxyl ions on alumina, in mole/cm², respectively.

As can be seen from Fig. 2, the plot of the logarithm of Γ_{H^+} or Γ_{OH^-} against

pH is in the linear relationship. The intersection of both straight lines means the equi-adsorption point and it is at pH 7.4, while the isoelectric point of the same alumina is at pH 9.0 as shown in Fig. 1.

It is clearly understood from the above facts that the isoelectric point should not be identified with the equi-adsorption point.

3. The Equilibrium Solubility Diagram in the Alumina-Water System

As mentioned in an earlier section of this paper, many researchers considered the isoelectric point as one of the characteristic values governing the reaction between collector ions and oxide surface, and therefore, they determined the isoelectric points for various kinds of oxide mineral. Several investigators also studied the fundamental problems concerning the dependence of the isoelectric point on the nature of mineral as well as the reason why the individual mineral has its own isoelectric point.
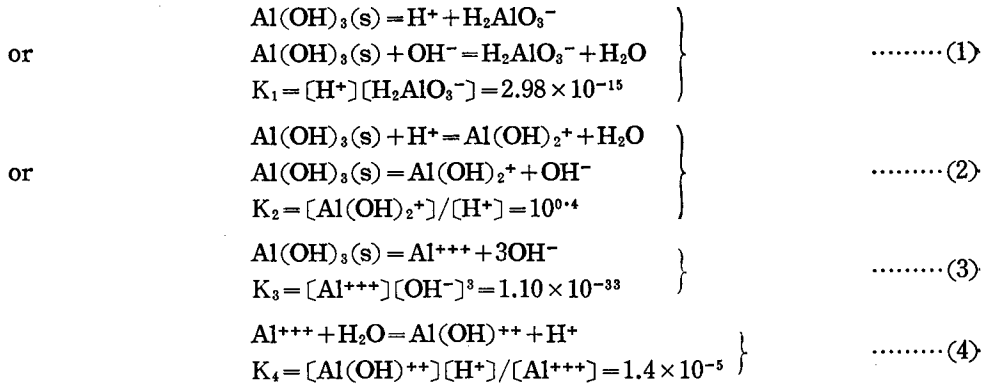
P. L. du Bruyn et al[10] investigated it by using Fe_2O_3 solid on the relation between the isoelectric point and the pH value of water at which a charge balance is established among the positively and negatively charged species formed from reactions between the constituent atoms of the oxide mineral and hydrogen or hydroxyl ions. Then, it was found that for Fe_2O_3 the isoelectric point agreed with the isoelectric pH as determined by the anions and cations of ferrous hydroxo-complexes in solution. But this concept has not been successfully applied to the other oxide systems. They also tried to consider that the isoelectric point for Ag_2O might agree with the pH of solution giving the minimum solubilty of the oxide.

The authors[11~13] have been studying flotation reactions with a concept that the adsorption of collector or depressant ion onto mineral surface should be principally due to the chemical affinity of the reaction between the constituent atom of mineral and collector or depressant ion.

Similarly, in order to investigate how closely the chemical affinities of conceivable reactions in the alumina-water system relate to the adsorption of hydrogen and hydroxyl ions on alumina, the ionic equilibrium is discussed in this section.

The thermodynamical data concerning the alumina-water system were published by W. M. Latimer[14], followed by K. H. Gayer et al[15] in detail in 1958.

The equations and equilibrium constants for the conceivable reactions in this system are as follows,

$$Al(OH)_3(s) = H^+ + H_2AlO_3^-$$

or $$Al(OH)_3(s) + OH^- = H_2AlO_3^- + H_2O \qquad \cdots\cdots\cdots(1)$$

$$K_1 = [H^+][H_2AlO_3^-] = 2.98 \times 10^{-15}$$

$$Al(OH)_3(s) + H^+ = Al(OH)_2^+ + H_2O$$

or $$Al(OH)_3(s) = Al(OH)_2^+ + OH^- \qquad \cdots\cdots\cdots(2)$$

$$K_2 = [Al(OH)_2^+]/[H^+] = 10^{0.4}$$

$$Al(OH)_3(s) = Al^{+++} + 3OH^-$$

$$K_3 = [Al^{+++}][OH^-]^3 = 1.10 \times 10^{-33} \qquad \cdots\cdots\cdots(3)$$

$$Al^{+++} + H_2O = Al(OH)^{++} + H^+$$

$$K_4 = [Al(OH)^{++}][H^+]/[Al^{+++}] = 1.4 \times 10^{-5} \qquad \cdots\cdots\cdots(4)$$

From the above equilibrium constants, the logarithms of the concentrations of the various species, $H_2AlO_3^-$, $Al(OH)_2^+$, Al^{+++}, and $Al(OH)^{++}$, are plotted as a function of pH of an aqueous solution in equilibrium with a hydrate of alumina, $Al(OH)_3$ solid.

$$\log [H_2AlO_3^-] = pH + \log K_1 \qquad \cdots\cdots\cdots(5)$$

$$\log [Al(OH)_2^+] = \log K_2 - pH \qquad \cdots\cdots\cdots(6)$$

$$\log [Al^{+++}] = \log K_3 - 3 \log K_w - 3\, pH \qquad \cdots\cdots\cdots(7)$$

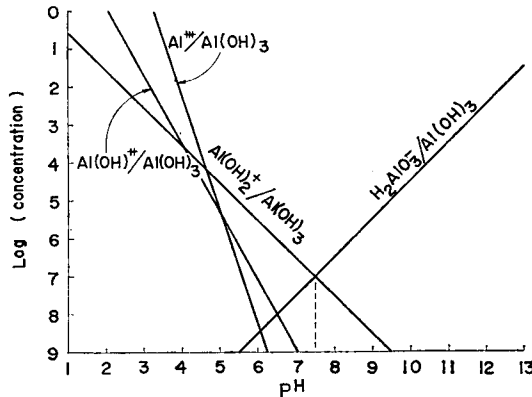$$\log [Al(OH)^{++}] = \log K_4 + \log K_3 - 3 \log K_w - 2\, pH \qquad \cdots\cdots\cdots(8)$$

Fig. 3. Variation of the concentration of various aluminum-bearing species with pH in aqueous solution in equilibrium with solid alumina.

From relations (5), (6), (7) and (8) the logarithmic concentration diagram for the alumina-water system was obtained as shown in Fig. 3. As can be seen in Fig. 3, for $[H_2AlO_3^-]$ a straight line of slope $+1$ is obtained, whereas for the other species, $[Al(OH)_2^+]$, $[Al(OH)^{++}]$, and $[Al^{+++}]$, straight lines having slopes of -1, -2 and -3 are obtained respectively.

4. The Equi-adsorption Point and the Equilibrium Solubility Diagram for the Alumina-Water System

It is seen from Fig. 2 that the equi-adsorption point of alumina is at pH 7.4. Fig. 3 shows that the intersection of the curves for $[H_2AlO_3^-]$ and $[Al(OH)_2^+]$ is at pH 7.5. It is quite interesting to note that the equi-adsorption point agrees exactly with the intersection of the curves for $[H_2AlO_3^-]$ and $[Al(OH)_2^+]$.

This fact shows that the adsorption mechanism of hydrogen and hydroxyl ions on alumina is closely associated with the reactions (1) and (2), which specify the concentrations of $H_2AlO_3^-$ and $Al(OH)_2^+$ in solution in equilibrium with solid $Al(OH)_3$. At pH 7.5 the concentrations of Al^{+++} and $Al(OH)^{++}$ are sufficiently negligible compared to the concentrations of $H_2AlO_3^-$ and $Al(OH)_2^+$. Thus, it can be clearly stated that the species, Al^{+++} and $Al(OH)^{++}$, have not any effect on the adsorption of hydrogen and hydroxyl ions at the pH range near the equi-adsorption point.

Although there may be various factors determining the adsorption process of hydrogen and hydroxyl ions on alumina, the chemical affinity of reaction (1) or (2) is porbably considered to be one of closely related factors.

Furthermore, in Fig. 3, the pH of the point where two curves for $[H_2AlO_3^-]$ and $[Al(OH)_2^+]$ meet each other corresponds to the pH of the solution giving the minimum solubility of a hydrate of alumina, $Al(OH)_3$. Therefore, it also can be said that the pH of the minimum solubility of oxide may agree with the equi-adsorption point rather than the isoelectric point for the alumina-water system.

5. Application to the Other Oxide System

It is important to know whether the same discussion as done on the alumina-water system is applicable to the other oxide-water system or not. For that purpose, the detailed thermodynamical information on the reactions in water between the atoms of the oxide concerned and hydrogen or hydroxyl ion must be fully available. For several oxides including SnO_2 whose thermodynamical data are somewhat sufficient, favorable results have been obtained.

6. Conclusion

As a part of the fundamental study on the mechanism of collector reaction onto oxide minerals in flotation, the adsorption of hydrogen and hydroxyl ions on alumina was surface-chemically investigated. Especially the equi-adsorption point defined here as a pH value of water where hydrogen and hydroxyl ions adsorb in equal amount was clearly shown.

Firstly, it was verified experimentally that the isoelectric point was not always in agreement with the equi-adsorption point.

Secondarily, the equi-adsorption point of alumina was also determined by considering the equilibrium solubility diagram which was obtained from thermodynamical information for several reactions in the alumina-water system.

Finally, it was concluded that the adsorption of hydrogen and hydroxyl ions on oxide minerals was closely related to the chemical affinity of reactions between the constituent atoms of mineral and hydrogen or hydroxyl ion.

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