

Adsorption of Hydrogen and Hydroxyl Ions on Oxide Mineral

By

Shigeru MUKAI and Takahide WAKAMATSU

(Received September 12, 1969)

The adsorption amount of hydrogen and hydroxyl ions on alumina in water was determined by the acid titration method which was theoretically well explained in this study. It was found that there should be a value of pH, defined here as the equi-adsorption point, at which hydrogen and hydroxyl ions were equal in adsorption amount on alumina. The adsorption isotherms of hydrogen and hydroxyl ions on alumina were expressed in the form of Freundlich isotherm. The equi-adsorption point for alumina was pH 7.4, while the isoelectric point for the same material was pH 9.0 by the electrophoresis measurement. The heat of immersion of alumina was also measured in water at various pH values. The pH dependence of the heat of immersion related closely with the adsorption of hydrogen and hydroxyl ions. The pH value where there is the minimum value in the heat of immersion coincided with the equi-adsorption point. Thus, it was confirmed that the equi-adsorption point should not always be in agreement with the isoelectric point.

1. Introduction

Concerning the reaction between collector ions and oxide minerals such as quartz, alumina, and iron oxides, it has been said that the electrokinetic potential (ζ -potential) of the oxide mineral and the ionic property of the collector reagent should play an important role in the adsorption process.¹⁾⁻³⁾ For example, cationic collectors adsorb onto the mineral surface in the pH range where the ζ -potential of the solid in water is negative, while anionic surfactants react in the pH region where the ζ -potential is positive. Therefore, the isoelectric point of minerals has been considered as a significant factor controlling the flotation behavior of oxide minerals. A number of researchers have determined isoelectric points for various minerals and then the adsorption of collector ions on mineral surface has been discussed from the ζ -potential of mineral.⁴⁾ This thought has been emphasized especially on the oxide mineral flotation.

On the other hand, with progress of the investigation on surface reaction

* Mineral Science and Technology

for various flotation systems, it has been pointed out that the reaction between collector ions and the oxide minerals, not to mention the sulfide minerals, could not simply be explained with the concept of ζ -potential.⁵⁾⁻⁷⁾ There has been many facts in which ionic surfactants adsorb onto the oxide mineral surface independently of the sign of ζ -potential. Therefore, the mechanism of the reaction between oxide mineral and surfactant ion has not yet been fully understood.

Accordingly, a study to elucidate the mechanism of the surfactant reaction onto the oxide minerals should be of value in establishing the principle of oxide flotation.

As the first step for the investigation of the reaction between the surface of oxide mineral and the collector ion, the behavior of hydrogen and hydroxyl ions which should be most closely related to the surface reaction were considered. A method to measure the adsorption amount of hydrogen and hydroxyl ions was first discussed and then the adsorption density of hydrogen and hydroxyl ions on the oxide mineral were determined to consider their adsorption process surface-chemically.

2. Discussions on potentiometric titration

The mineral particles suspended in an aqueous solution generally have their own buffer action with a certain value of pH. For determining the adsorption amount of adsorbate there is a usual method which involves measuring the difference in concentration of the adsorbate in the solution before and after adding the adsorbent. However, it is impossible to use the conventional method in the case of the adsorption of hydrogen and hydroxyl ions on the mineral surface in the aqueous solution, because water itself is the source of supplying hydrogen and hydroxyl ions.

In this study the potentiometric titration for the solution of mineral particles suspension was employed using HCl as a titrant. Parks⁸⁾ was the first man who tried to study the behavior of hydrogen and hydroxyl ions onto the mineral surface by using the potentiometric titration for the mineral suspension. Thereafter, many researchers have continued the flotation study by employing the potentiometric technique.⁹⁻¹¹⁾ However, the discussions on the titration results conducted so far have been still qualitative because of the lack of the theoretical consideration on the titration curves. The interpretation for the results of the potentiometric titration has been inadequate. The authors tried, first of all, the theoretical considerations on the potentiometric titration curves for the solution of mineral particle suspension.

In order to determine the adsorption amount of hydrogen and hydroxyl ions

onto the mineral surface by means of the potentiometric titration, two titration experiments, namely one for a solution without particles suspension and the other for a solution with particle suspension, were conducted. The two titration curves will be theoretically discussed in the case where the amount of titrant is very small compared with the volume of suspension solution.

The acid titration for a solution without particles suspension is considered. Figure 1 shows a titration curve added with HCl for the solution containing only some amount of alkali such as NaOH.

If x is the amount of the acid (HCl) required for varying the pH value of the solution from pH_0 to pH_1 , then the following relations will be obtained;

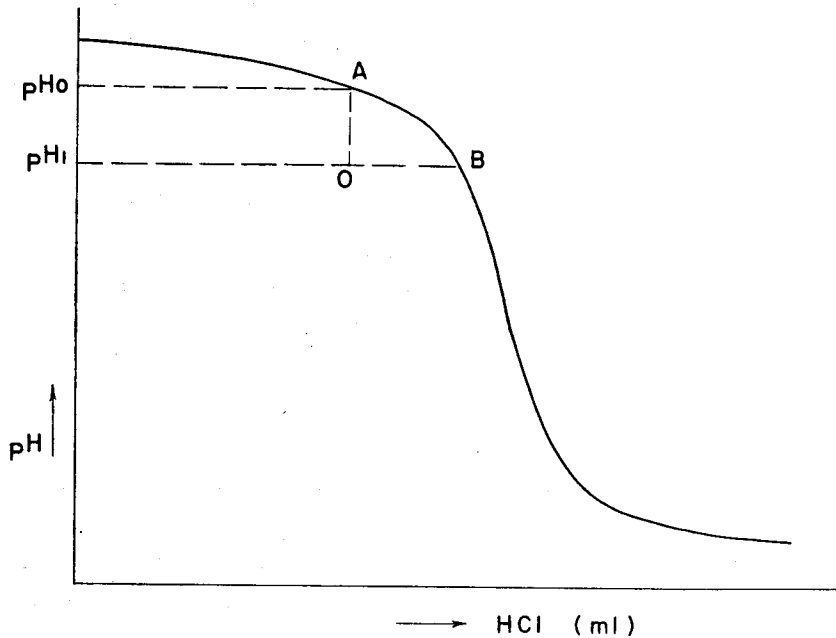


Fig. 1. Titration curve for water.

$$\left. \begin{aligned}
 [H^+]_1 &= [H^+]_0 + \xi a \\
 [OH^-]_1 &= [OH^-]_0 - \xi(x-a)
 \end{aligned} \right\} \dots\dots\dots (1)$$

and

$$[OH^-]_0 [H^+]_0 = [OH^-]_1 [H^+]_1 = K_w,$$

where a represents the amount of acid remaining in the solution as hydrogen ion out of the whole amount of the acid added, x , while $(x-a)$ represents the amount of

the acid consumed by hydroxyl ion to become water. ξ is a parameter which converts the amount of acid addition into the concentration unit depending on the volume of the solution used in the experiments. K_w is the ion product of water.

From the relation in (1), the following formula is obtained.

$$x = \overline{OB} = \frac{1}{\xi} ([H^+]_1 - [H^+]_0) \left(\frac{K_w}{[H^+]_0 [H^+]_1} + 1 \right) \dots\dots\dots (2)$$

It was confirmed that the above formula fairly represents the actual titration curves obtained in the experiments.

Figure 2 shows a titration curve for the solution with particles suspension. In the same way as before, x was assumed to be the amount of acid necessary for changing the pH value of the solution from pH_0 to pH_1 . The following relations are obtained;

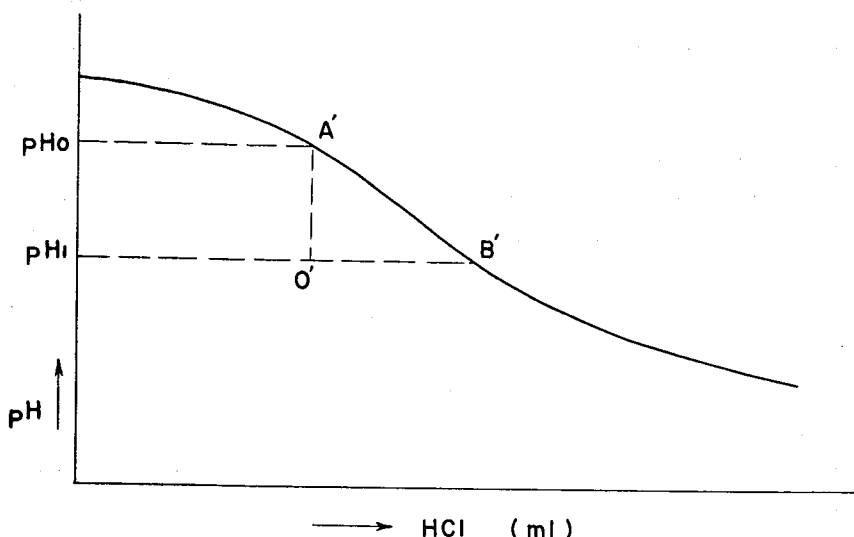


Fig. 2. Titration curve for solution of particle suspension.

$$\left. \begin{aligned} x &= a + \Delta\Gamma_{H^+} + b \\ [H^+]_1 &= [H^+]_0 + \xi a \\ [OH^-]_1 &= [OH^-]_0 + \xi \Delta\Gamma_{OH^-} - \xi b \end{aligned} \right\} \dots\dots\dots (3)$$

and

$$[H^+]_1 [OH^-]_1 = [H^+]_0 [OH^-]_0 = K_w, \dots\dots\dots (4)$$

where

$$\Delta\Gamma_{H^+} = \Gamma_{H^+}_1 - \Gamma_{H^+}_0, \quad \Delta\Gamma_{OH^-} = \Gamma_{OH^-}_0 - \Gamma_{OH^-}_1.$$

The first equation in the above relations means that the amount of acid added is distributed into three portions, namely the first portion remaining in the solution as hydrogen ion, the second portion contributing to the increase in the adsorption

of hydrogen ion onto the mineral, and the third portion combining with hydroxyl ion to become water. From the above relations, the following expression for x is derived;

$$x = \overline{OB'} = \frac{1}{\xi} \left\{ ([H^+]_1 - [H^+]_0) + K_w \left(\frac{1}{[H^+]_0} - \frac{1}{[H^+]_1} \right) + \xi (\Delta\Gamma_{H^+} + \Delta\Gamma_{OH^-}) \right\} \quad (5)$$

Parks and the others considered the isoelectric point of mineral as a point where hydrogen and hydroxyl ions were equal in adsorption amount on the mineral surface. Under this assumption, they discussed the adsorption of hydrogen and hydroxyl ions from the potentiometric titration experiments.

However, it is not always considered that the isoelectric point should be a point where hydrogen and hydroxyl ions adsorb in equal amount because there is an inherent surface charge on the mineral surface.

The authors have worked on how to determine the equi-adsorption point, defined here as a pH value where hydrogen and hydroxyl ions adsorb in equal amount, by making use of the titration technique. Eventually, the procedure by which the equi-adsorption point is determined was found as described in the following parts of this section.

Two beakers having equal amount of alkaline solution in the exact same conditions (the same pH and temperature) are prepared. Mineral particles are suspended in one of the two solutions and then titrated with the acid, while the other solution which does not contain the mineral particles is titrated with the acid.

With this procedure, the two titration curves are always obtained as shown in Figure 3. The pH value of the solution with mineral suspension slightly shifts to pH_0' from pH_0 which is a pH value before adding the mineral particles. The curve I is the titration curve for the solution without the mineral particles suspension. The curve II is the titration curve for the solution of the mineral particles suspension. The both curves, I and II, intersect each other at a certain value of pH (pH_1 in Figure 3).

The relation between pH_0 and pH_0' was discussed as follows. At first it is assumed that the alkalinity of the solution, pH_0 , is adjusted by adding only NaOH in pure water. Then, the charge balance is expressed as follows;

$$[H^+]_0 + [Na^+] = [OH^-]_0 \quad \dots\dots\dots (6)$$

When the mineral particles are added in the solution, the charge balance is;

$$[Na^+] + [H^+]_0 + \xi \Gamma_{H_0^{+'}} = [OH^-]_0' + \xi \Gamma_{OH_0^{-}'} \quad \dots\dots\dots (7)$$

where $\Gamma_{H_0^{+'}}$ and $\Gamma_{OH_0^{-}'}$ represent the adsorption amounts of hydrogen and

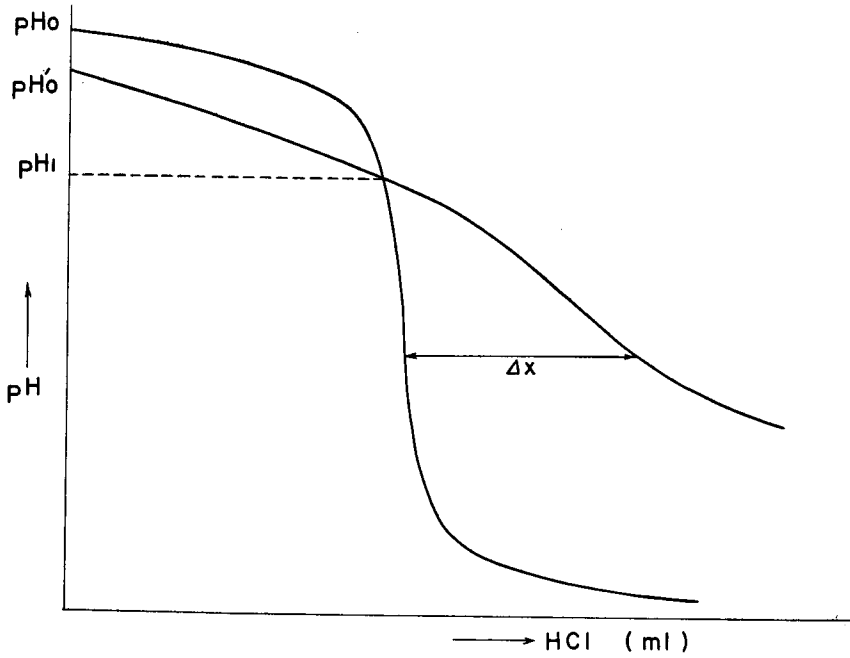


Fig. 3. Titration curves;
 I: for water
 II: for solution of particle suspension.

hydroxyl ions onto mineral surface at pH_0' , respectively.

From (6) and (7), the following relation is derived;

$$[OH^-]_0 - [OH^-]' + [H^+]_0' - [H^+]_0 = \xi \Gamma_{OH_0'} + \xi \Gamma_{H_0'} \dots\dots\dots(8)$$

Equation (8) states the relation between pH_0 and pH_0' .

Then, using equations (2), (5), and (8), for the pH at the intersection of lines, I and II, the following relation is finally obtained.

$$\Gamma_{H_1^+} - \Gamma_{OH_1^-} = 0 \dots\dots\dots(9)$$

The difference between two curves at arbitrary pH is;

$$\Gamma_{H^+} - \Gamma_{OH^-} = \Delta x \dots\dots\dots(10)$$

Thus, it is clearly understood that the equi-adsorption point can be obtained from the intersection of curves, I and II. Further, it is surely recognized by many experiments that the pH value of the intersection is constant regardless of pH_0 , the amount of the mineral particles, and the volume of the solution, as far as the same suspension material is used in the test. This fact must be especially emphasized.

3. Titration experiments

Titration experiments were carried out in the nitrogen atmosphere at fixed temperature 25°C. The schematic illustration for the experiment is shown in Figure 4. Alumina which was provided by Union Carbide as "Linde A" was used.

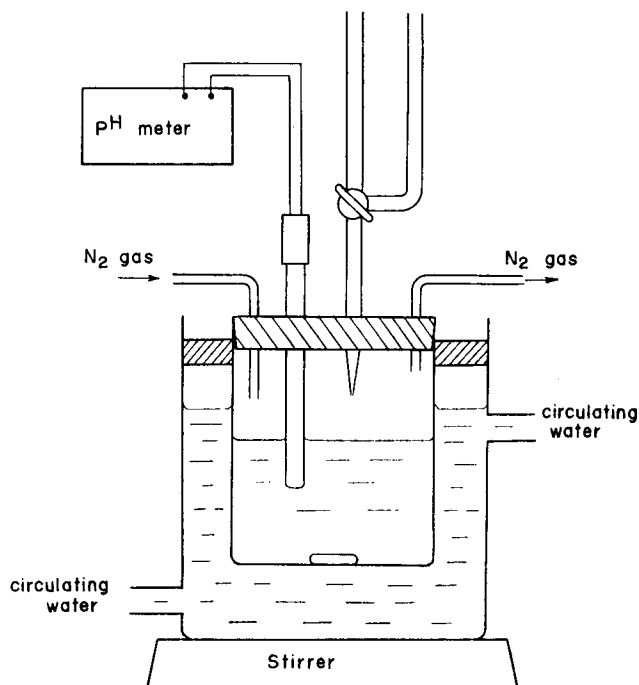


Fig. 4. Schematic representation of titration apparatus.

The BET surface area measurement showed the surface area to be 15 m²/g. The pH value of the solution was measured by Beckman 1019 type pH meter.

In determining the titration curve corresponding to curve I in Figure 3, pH of the solution is measured promptly after each small amount of the acid is added, because there is no particle suspension in the solution. On the other hand, in order to obtain the titration curve corresponding to curve II in Figure 3, it is required a certain length of time to measure pH value at equilibrium after each addition of acid, because there exists a ion adsorption process at the water-mineral interface. In this study, 20 minutes stirring followed by 5 minutes settling was taken each time after a small amount of acid (HCl) was added.

Figures 5 and 6 show two experiments in which 4 grams of alumina and 200 cc of solution were used, each of them being slightly different in their experimental condition from each other. Figure 5 is result of the titration experiment in which

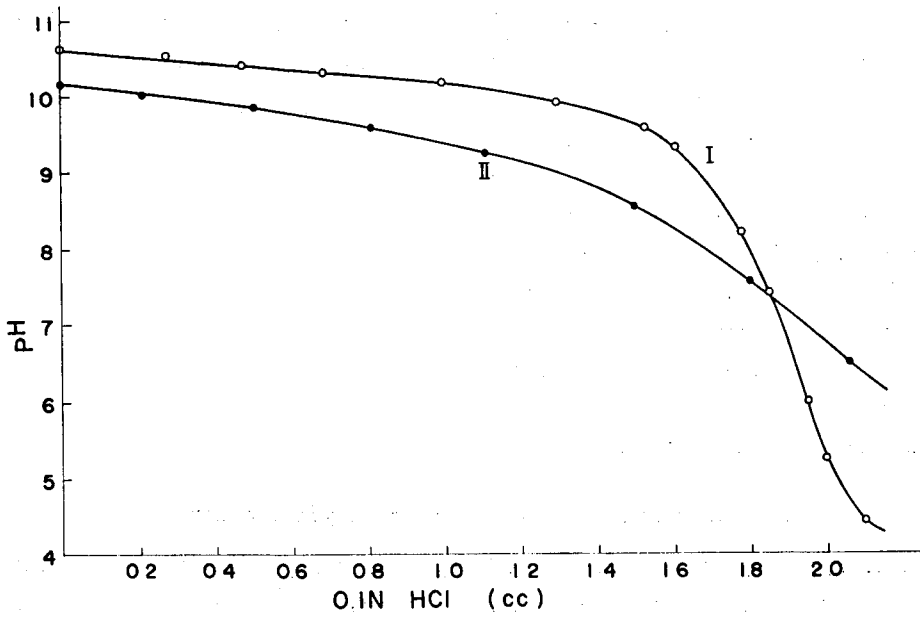


Fig. 5. Titration curves for water the pH value of which was initially adjusted at 10.6,
 I: for water
 II: for solution of particle suspension.

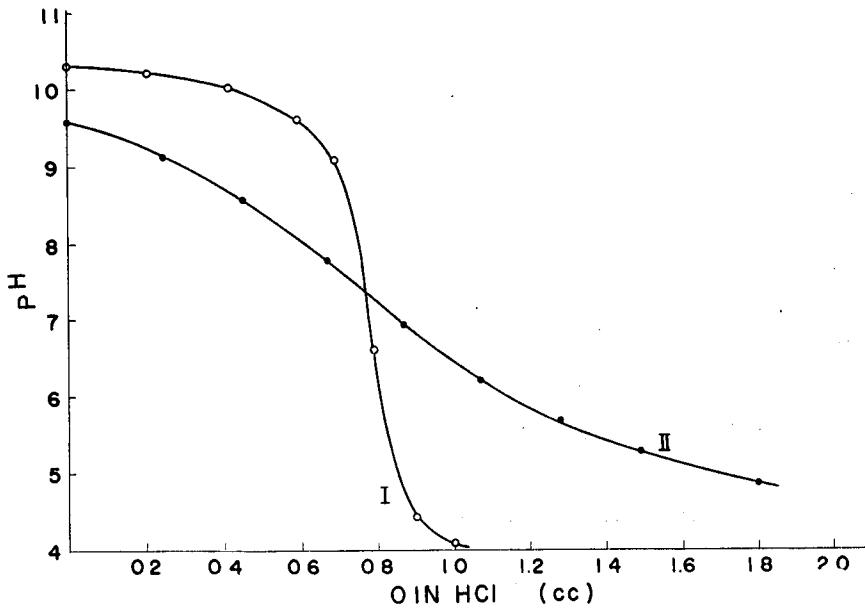


Fig. 6. Titration curves for water the pH value of which was initially adjusted at 10.3,
 I: for water
 II: for solution of particle suspension.

pH_0 of the solution without the mineral particles suspension was adjusted at 10.6. Figure 6 is the result of the titration test in which pH_0 was 10.3.

As can be seen from Figures 5 and 6, it was recognized that the pH at the intersection of the two titration curves is constant, namely 7.4. It was also confirmed that the pH value of 7.4 at the intersection of the two titration curves was held even in the other experiments whose solution amount and particles suspension amount were different one from another.

From the above results, it is especially emphasized that the pH at the intersection of two titration curves, I and II, shown in Figure 3 should be unchanged regardless of the experimental conditions. Further, the equi-adsorption point where hydrogen and hydroxyl ions adsorb in equal amount onto the mineral surface should be $\text{pH}=7.4$ for the alumina used in this study.

4. Adsorption of hydrogen and hydroxyl ions

According to equation (10), the difference between the Curves I and II in Figure 3, at a given pH value, x in acid amount, represents the difference in the adsorption amount between hydrogen and hydroxyl ions.

Figures 7 and 8 show the difference between Γ_{OH^-} and Γ_{H^+} as a function of pH,

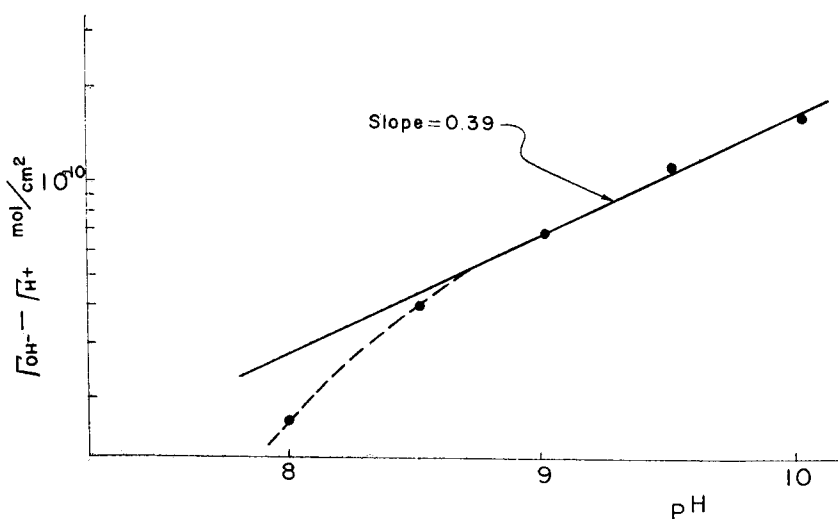


Fig. 7. The plot of $\Gamma_{\text{OH}^-} - \Gamma_{\text{H}^+}$ as a function of pH.

which were obtained from the results of Figures 5 and 6. As can be seen from Figures 7 and 8, the value of $\Gamma_{\text{OH}^-} - \Gamma_{\text{H}^+}$ or $\Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-}$ become zero at pH region near 7.4 while they become larger in alkaline or acidic region. In the fairly alkaline or acidic region, the plot of the logarithm of $(\Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-})$ or $(\Gamma_{\text{OH}^-} - \Gamma_{\text{H}^+})$

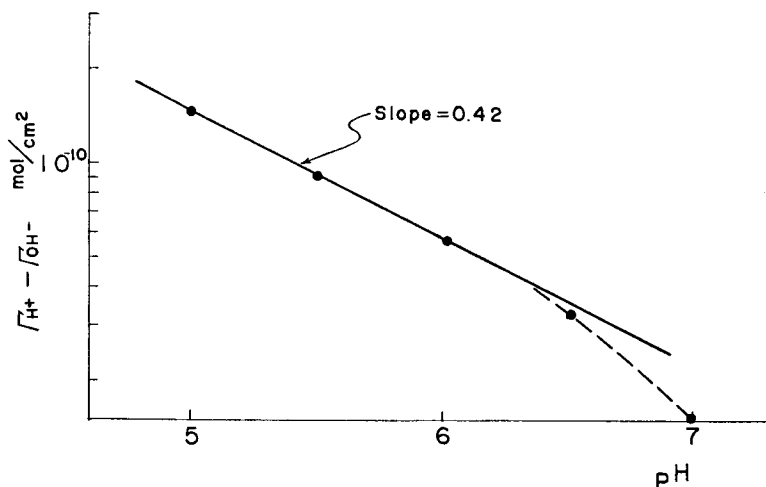


Fig. 8. The plot of $\Gamma_{H^+} - \Gamma_{OH^-}$ as a function of pH.

against pH is in the linear relationship. The slopes of the straight lines are 0.39 for the alkaline region and 0.42 for the acidic region. In these regions, it is considered that the adsorption amount of one species of ion is very small compared with that of the other. Therefore, in determining the isotherms for the hydrogen and hydroxyl ion it was assumed that the relation between the adsorption amount and the concentration is expressed for each ion in the following form;

$$\begin{aligned} \Gamma_{H^+} &= K_{H^+}[H^+]^{0.42} \\ \Gamma_{OH^-} &= K_{OH^-}[OH^-]^{0.39} \end{aligned}$$

The values of K_{H^+} and K_{OH^-} were determined through the least square method using some values of $(\Gamma_{OH^-} - \Gamma_{H^+})$ and $(\Gamma_{H^+} - \Gamma_{OH^-})$ at several pH values plotted in Figures 7 and 8.

As a consequence, the isotherms for the adsorption of hydrogen and hydroxyl ions onto alumina surface were obtained as follows;

$$\begin{aligned} \Gamma_{H^+} &= 2 \times 10^{-8} [H^+]^{0.42} \\ \Gamma_{OH^-} &= 5.8 \times 10^{-9} [OH^-]^{0.39} \end{aligned} \dots\dots\dots(11)$$

Figure 9 shows the above two isotherms in the log Γ - pH plot, which are characterized by Freundlich isotherm type.

From the above results, it is concluded that the adsorption isotherms of hydrogen and hydroxyl ions should be determined through the titration method and that the isotherms for the adsorption of hydrogen and hydroxyl ion onto alumina surface are represented in the Freundlich equation.

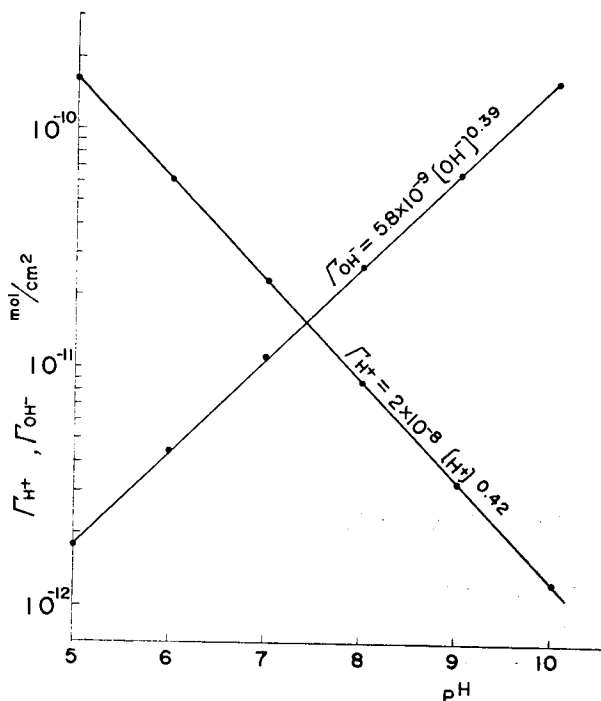


Fig. 9. Adsorption isotherms of hydrogen and hydroxyl ions for alumina.

5. Equi-adsorption point and isoelectric point

As mentioned in an earlier section of this paper, several researchers consider that the hydrogen and hydroxyl ions adsorb in equal amount at the isoelectric point where ζ -potential is zero.¹²⁾ Much literature show that the isoelectric point for alumina is $\text{pH}=8.9\sim 9.2$ ¹³⁾, while the equi-adsorption point for alumina used in this experiment was determined to be 7.4.

Accordingly, the electrophoresis measurement for alumina used in this study was made by Zeta meter in order to obtain its isoelectric point. The result of the electrophoresis measurement for alumina is shown in Figure 10.

As can be seen in Figure 10, the alumina sample in this study has its isoelectric point at $\text{pH}=9.0$, different from the equi-adsorption point.

From the above facts it is emphasized that the isoelectric point should not be identified with the equi-adsorption point where hydrogen and hydroxyl ions adsorb onto the mineral surface in equal amount. Furthermore, it can be said that this fact should afford a new aspect on the surface-chemistry study.

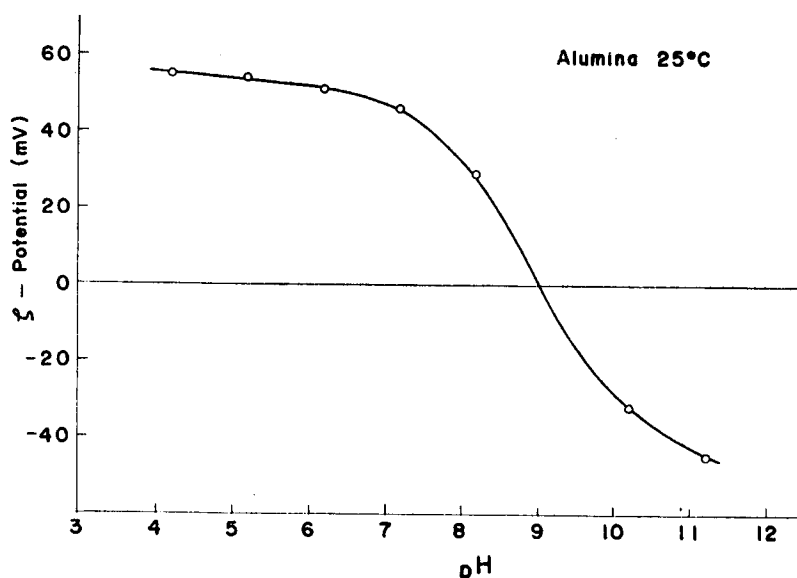


Fig. 10. ζ -potential of alumina particles in water as a function of pH.

6. Heat of immersion and equi-adsorption point

The heat of immersion in the alumina-water system is considered to be closely related to the adsorption of hydrogen and hydroxyl ions on alumina. Therefore, the pH dependence of the heat of immersion in the alumina-water system was investigated using Oyodenki CM-204 type micro calorimeter. A given amount of the alumina powder and a given volume of water were put into separate vessels in the calorimeter and allowed to equilibrate with temperature 25°C for 17-24 hours. Then, the powder was immersed into the water.

Figure 11 shows the relation between the heat of immersion and the equilibrium pH of water after immersing the alumina powder.

As can be seen in Figure 11, the heat of immersion in the alumina-water system is pH dependent, namely, about 93 erg/cm² at pH=4, 75 erg/cm² in the neutral pH range, and about 85 erg/cm² at pH=10. There is a minimum in the immersional heat at pH=7.5 or 7.4, which coincides with the equi-adsorption point previously obtained.

Figure 12 indicates the sum of the adsorption density of hydrogen and hydroxyl ions on alumina as a function of pH. At the equi-adsorption point the total sum of the hydrogen and hydroxyl ions adsorption is minimum. From the results in Figures 11 and 12, it is noticed that the heat of immersion should be closely related with the adsorption of hydrogen and hydroxyl ions. Further, the immersional

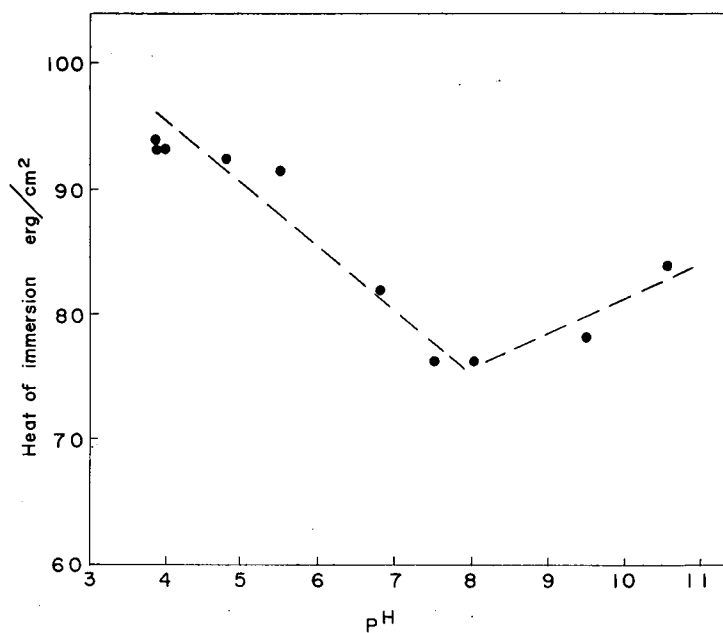


Fig. 11. Heat of immersion in alumina-water system.

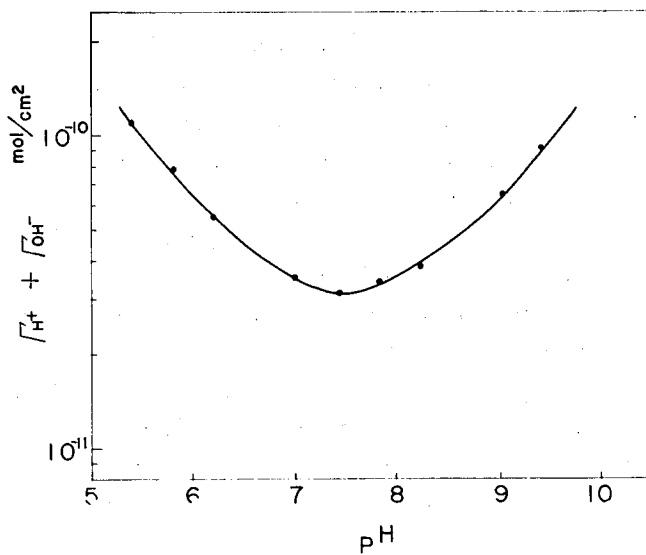


Fig. 12. The plot of $\Gamma_{H^+} + \Gamma_{OH^-}$ as a function of pH.

heat measurements support that the equi-adsorption point in the alumina-water system should be at $\text{pH}=7.4\sim 7.5$ and should be different from the isoelectric point conventionally used in electro-surface chemistry.

7. Summary

As a part of the fundamental study on the reaction between the surfaces of the oxide mineral and the collector ions, the adsorption of hydrogen and hydroxyl ions onto the mineral surface was considered from the view point that the hydrogen and hydroxyl ions should play an important role in the surface reaction process.

Alumina was used as a test sample. The adsorption amount of hydrogen and hydroxyl ions on alumina was determined by the acid titration method which was theoretically well discussed in this study. It was found that there should be a value of pH at which hydrogen and hydroxyl ions were equal in adsorption amount on alumina. Further, it was shown both experimentally and theoretically that the pH value defined in the present paper as the equi-adsorption point, was a value of pH at the intersection of two acid titration curves, one for a solution without alumina particles and the other for a solution with the particle suspension.

The adsorption isotherm of hydrogen and hydroxyl ions on alumina were expressed in the form of Freundlich isotherm;

$$\begin{aligned}\Gamma_{H^+} &= 2 \times 10^{-8} [H^+]^{0.42} \\ \Gamma_{OH^-} &= 5.8 \times 10^{-9} [OH^-]^{0.39}\end{aligned}$$

The equi-adsorption point for alumina was pH 7.4, while the isoelectric point for the same material was pH 9.0 by the electrophoresis measurement.

The heat of immersion of alumina was also measured in water at various pH values. The heat of immersion of alumina into water decreases with decreasing acidity up to pH 7, reaches a minimum value at about pH 7.5, and then increases with increasing alkalinity. The pH value where there is the minimum value in the heat of immersion coincides with the equi-adsorption point. It was shown that the variation in the heat of immersion relates closely with the adsorption of hydrogen and hydroxyl ions.

Thus, the above adsorption measurement and the immersionsal heat measurement support that the equi-adsorption point in the alumina-water system should be at pH 7.4 and should not always be in agreement with the isoelectric point.

References

- 1) I. Iwasaki, S.R.B. Cooke and H.S. Choi: *Trans. Am. Inst. Mining Met. Engrs.*, Vol. 217, p. 237 (1960)
- 2) I. Iwasaki, S.R.B. Cooke and A.F. Colombo: *Report of Investigation, No. 5593, U.S. Bureau of Mines* (1960)
- 3) G. Purcell: *PhD Thesis, Pennsylvania State University* (1960)
- 4) G.A. Parks: *Chemical Review*, Vol. 65, p. 177 (1965)

- T.W. Healy, D.W. Fuerstenau: *J. Colloid Science*, Vol. 20, p. 376 (1965)
G.A. Parks: *Advances in Chemistry Series*, No. 67, p. 121 (1967)
- 5) M.E. Wadsworth, A.S. Peck and L.H. Raby: *Trans. Am. Inst. Mining Met. Engrs.*, Vol. 235, p. 301 (1966)
 - 6) G. Purcell and S.C. Sun: *Trans. Am. Inst. Mining Met. Engrs.*, Vol. 226, p. 6 (1963)
 - 7) I. Iwasaki, S.R.B. Cooke and Y.S. Kim: *Trans. Am. Inst. Mining Met. Engrs.*, Vol. 223, p.113 (1962)
 - 8) G.A. Parks and P.L. de Bruyn: *J. Phys. Chem.*, Vol. 66, p. 967 (1962)
 - 9)-11) PhD Thesis, Massachusetts Institute of Technology (1962-6)
 - 12) "Froth Flotation" 50th anniversary volume, *Am. Inst of Mining Met. Engr.*, New-York, p. 91 (1962)
 - 13) R. Fricke, H. Keefer: *Z. Naturforsch.*, 4A, p. 76 (1949)
P.G. Johansen, A.S. Buchanan: *Australian J. Chem.*, Vol. 10, p. 392 (1957)
H.J. Modi, D.W. Fuerstenau: *J. Phys. Chem.*, Vol. 61, p. 649 (1957)
P.G. Johansen, A.S. Buchanan: *Australian J. Chem.*, Vol. 10, p. 398 (1957)
J.A. Yopps, D.W. Fuerstenau: *J. Colloid Science*, Vol. 19, p. 61 (1964)