# *The Effects of pH on the Flocculation of Quartz Aqueous Suspensions*

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Control of the state of dispersion or flocculation of mineral suspension is widely required for proper operation of many chemical engineering processes. It is well known that, especially in the case where metal ions are dissolved, the pH of the solution is closely related to the stability of suspensions. From this point of view, the effects of pH on the flocculation of quartz aqueous suspensions containing a cation, such as $Ba^{2+}$, $Fe^{3+}$ or $Cu^{2+}$, respectively, are investigated by means of electrokinetic measurements.

## Experimental

Quartz suspensions, 6% by weight, were provided for the flocculation experiments. A monocrystalline quartz was ground by a laboratory roll crusher, and it was washed with hydrochloric acid; the washing was followed by successive decantation with distilled water until no $Cl^-$ could be detected, and the quartz powder under 150 mesh was well reground in an agate mortar after drying. $Ba^{2+}$, $Fe^{3+}$ or $Cu^{2+}$ was supplied by $BaCl_2$, $FeCl_3$ or $CuSO_4 \cdot 5H_2O$ in reagent grade, respectively. The pH of solution was adjusted with hydrochloric acid or sodium hydroxide and measured by a glass electrode pH meter. The degree of flocculation was evaluated by measuring the transparency of suspensions, a Hitachi EPO-B photoelectric photometer was available for transparency measurements. The $\zeta$ potential of quartz in the solution containing $Fe^{3+}$ or $Cu^{2+}$ was measured by a microscopic electrophoresis cell, considering the fact that, for the system in which insoluble hydroxide is formed, the condition of streaming potentential method made on relatively coarse particles may differ from that of flocculation experiment carried out on the suspensions containing fine particles. For the solution of $Ba^{2+}$, on the other hand, the streaming potential method was adopted.

The quartz in the streaming potential measurements is the 48/65 mesh fraction, and the apparatus is the same as that used by Gaudin and Fuerstenau[1].

**The Effects of pH on the Flocculation of Quartz Suspensions Containing $Ba^{2+}$.** — Fig. 1 shows transparency-time curves under various pH of the suspension containing $Ba^{2+}$ of 1 mmol./l. in concentration. The abscissa is the elapsed time after shaking the suspension, the ordinate being

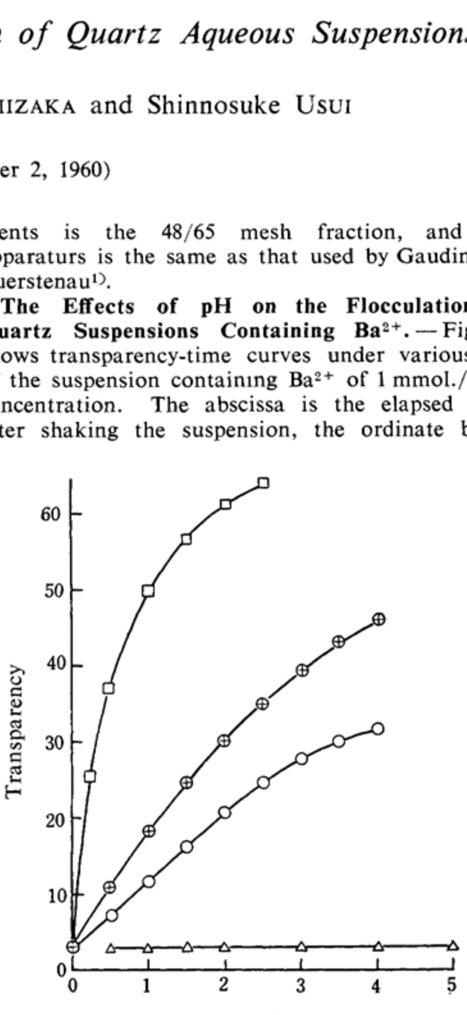

Fig. 1. Transparency-time curves of quartz suspension under various pH at the concentration of $BaCl_2$ 1.0 mmol./l.

- △ pH=3.0, 6.8, 8.8
- ○ pH=10.8
- ⊕ pH=11.0
- □ pH=12 or more

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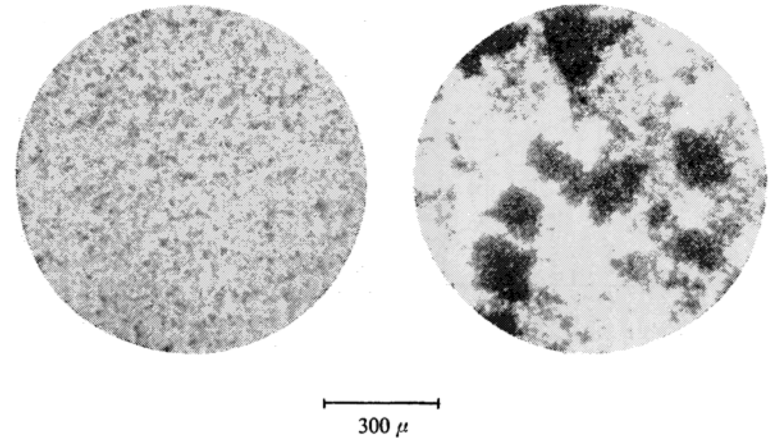
[1] A. M. Gaudin and D. W. Fuerstenau, *Min. Eng.*, 7, 66 (1955).



(a)
BaCl$_2$ 10 mmol./l., pH 5.0

(b)
BaCl$_2$ 10 mmol./l., pH 11.5

Fig. 2. Photomicrographs of flocs.

the degree of flocculation. From this figure it can be seen that the degree of flocculation becomes stronger with increasing pH in alkaline solutions. The flocculation in high pH is characterized by the formation of gel-like flocs. When the concentration of Ba$^{2+}$ is increased to more than 3 mmol./l., which is the flocculation value of Ba$^{2+}$ for the quartz suspension adopted at pH 7, the flocculation of the suspension is also observed in the acidic side. The flocculation in acidic solution, however, is relatively weak and no gel-like floc formation is observed. Fig. 2 shows the photomicrographs of flocs formed at the concentration of Ba$^{2+}$ 10 mmol./l.; Figs. 2a and 2b show flocs at pH 5.0 and pH 11.5, respectively. The flocculation of the quartz suspension disappears with decrease of the Ba$^{2+}$ concentration even in the solution of high pH, and the critical Ba$^{2+}$ concentration for flocculation is found to be 0.6 mmol./l. at pH 11.0. The critical Ba$^{2+}$ concentration decreases with increasing pH of the solution. When the pH is lowered to that of the acidic side the critical Ba$^{2+}$ concentration is also decreased, and at pH about 2 flocculation occurs without the addition of Ba$^{2+}$.

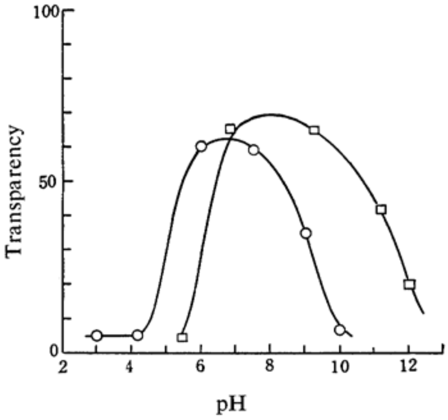


Fig. 3. Transparency at 5 min. after preparation of suspensions containing Fe$^{3+}$ or Cu$^{2+}$ as a function of pH.

○ Fe$^{3+}$ 0.4 mmol./l.
□ Cu$^{2+}$ 4.0 mmol./l.

**The Effects of pH on the Flocculation of Suspensions Containing Fe$^{3+}$ or Cu$^{2+}$.** — In the suspensions containing Fe$^{3+}$, no visible flocculation takes place in the range of low pH even though the Fe$^{3+}$ concentration reaches 0.4 mmol./l. However, the addition of sodium hydroxide to the above suspension produces a violent flocculation at about neutral pH. This flocculation is weakened, however, by the increase of pH and dissappears at the pH region higher than 10. Fig. 3 gives the relation between the transparency at 5 min. after shaking the suspension and pH of the solution containing Fe$^{3+}$ of 0.4 mmol./l. in concentration. For the suspension containing Cu$^{2+}$, 4 mmol./l., a remarkable flocculation takes place in the pH range of $6\sim12$. This is also illustrated in Fig. 3. It is always observed in the above experiments that the upper solution appearing after sedimentation of flocs is colorless and transparent, and the sediment with color of the hydroxide of the respective ion is formed, such as light brown for Fe$^{3+}$ and light blue for Cu$^{2+}$. The deflocculation of the suspensions occurs when the pH exceeds 10 for Fe$^{3+}$ and 12 for Cu$^{2+}$. On the other hand, in the suspension containing Ba$^{2+}$ the violent flocculation still takes place even in the pH region higher than 12.

These observations seem to indicate that the pH range in which the violent flocculation occurs is related to the solubility of the hydroxide of the ion involved; the larger the solubility of the hydroxide, the higher pH range where the flocculation is maintained is expected.

**ζ Potential.**—ζ Potential of quartz in the solutions of various concentrations of Ba$^{2+}$, i. e. 0.1, 0.2 and 1.0 mmol./l., as a function of pH is given in Fig. 4. The ζ potential at pH 11 in the presence of Ba$^{2+}$ of 0.6 mmol./l., the critical concentration for the flocculation, is also plotted in the same figure. Fig. 5 represents the ζ poten-

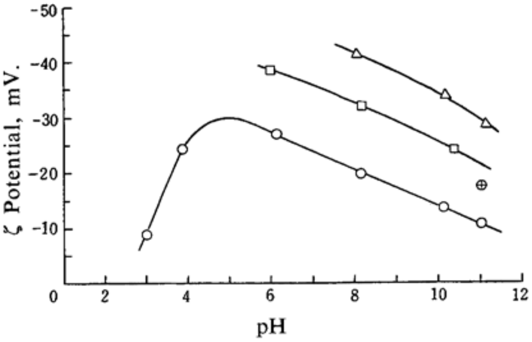


Fig. 4. Influence of pH on ζ potential of quartz in $BaCl_2$ solutions.

△ $BaCl_2$ 0.1 mmol./l.
□ $BaCl_2$ 0.2 mmol./l.
⊕ $BaCl_2$ 0.6 mmol./l.
○ $BaCl_2$ 1.0 mmol./l.

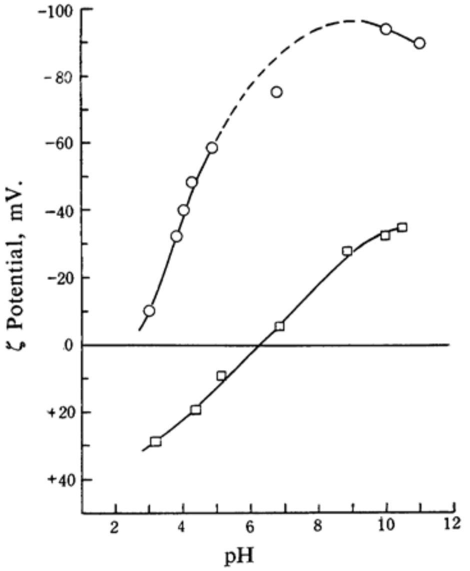


Fig. 5. ζ Potential of quartz in the absence or presence of $Fe^{3+}$ as a function of pH.

○ Absence of $Fe^{3+}$
□ $Fe^{3+}$ 0.4 mmol./l.

tial of quartz in the solutions containing only hydrochloric acid or sodium hydroxide and $Fe^{3+}$, 0.4 mmol./l., as a function of pH. From these figures it can be seen that the ζ potential decreases with increasing pH in alkaline solution at the respective $Ba^{2+}$ concentration, on the other hand, its value is considered to be determined mainly by $H^+$ in acidic solution. Gaudin and Fuerstenau[1] have shown that, in the streaming potential study made on 48/65 mesh quartz, the reliable values of the ζ potential were obtainable in the solution over $10^{-4}$ in ionic strength, below which it was necessary to consider the effect of surface conductivity. In the present investigation, the effect of surface conductivity was not appreciated, so that in Fig. 5 the region of lower ionic strength was expressed by a dotted line; if the correction is made, higher negative potential values would be expected. In the absence of $Fe^{3+}$, the isoelectric point of quartz seems to be in the neighbourhood of pH 2.5. On the other hand, the isoelectric point shifts to higher value of pH, i.e. about pH 6, in the presence of $Fe^{3+}$.

## Discussion

The stability of lyophobic colloids or suspensions depends upon the energy of interaction between two approaching particles. According to Verwey and Overbeek[2] the energy is composed of electrical repulsion and long range van der Waals attraction. For a given suspension the attraction is assumed to be constant while the repulsion changes with the electrolyte content of the system. These concepts will lead us to the prediction that the violent flocculation of the quartz suspension containing $Ba^{2+}$ in alkaline solution is due to the decrease of electrical repulsion. Verwey and Overbeek have calculated the repulsive potential of interaction between two flat double layers in the solution containing a species of binary electrolyte, and Eq. 1 has been obtained as the repulsive potential per unit area if the interaction is not so strong;

$$\left.\begin{aligned} V_R &= (64n\boldsymbol{k}T/\kappa)\gamma^2 \exp(-2\kappa d) \\ \kappa &= (8\pi ne^2v^2/\varepsilon\boldsymbol{k}T)^{1/2} \\ \gamma &= \{\exp(z/2)-1\}/\{\exp(z/2)+1\} \\ z &= ve\psi_0/\boldsymbol{k}T \end{aligned}\right\} \quad (1)$$

where $n$ is the number of ions per $cm^3$ far from the surface, $\boldsymbol{k}$ the Boltzmann constant, $T$ the absolute temperature, $e$ the elementary charge, $v$ the valency of counter ion, $\varepsilon$ the dielectric constant, $\psi_0$ the surface potential and $d$ the half-distance of separation.

Eq. 1, however, cannot be applied to the system in which more than two species of counter ions of different valency is involved. It is difficult to obtain a general formula representing the repulsive potential energy, but the repulsive potential can be expressed as Eq. 2[3] if ζ potential is not so high;*

$$\left.\begin{aligned} V_R &= (\varepsilon/2\pi)\kappa\zeta^2 \exp(-2\kappa d) \\ \kappa &= (4\pi e^2\sum n_i v_i^2/\varepsilon\boldsymbol{k}T)^{1/2} \end{aligned}\right\} \quad (2)$$

Thus, the repulsive potential is directly related to $\kappa$ and ζ. As indicated in Fig. 1, a remarkable flocculation takes place at pH 11 (NaOH,

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[2] E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids", Elsevier, Amsterdam, (1948).

[3] S. Usui, *J. Mining and Metallurgical Inst. Japan, (Nippon Kogio Kaishi)*, **75**, 1025 (1959).

* On the system containing a binary electrolyte, it is calculated that Eq. 2 gives the value of 1.0~1.1 times the one evaluated from Eq. 1 in the range of $Z(=ve\zeta/\boldsymbol{k}T$ for Eq. 2$)=0\sim1.5$.

1 mmol./l.), while no flocculation appears at pH 3 (HCl, 1 mmol./l.) despite of the same concentration of $Ba^{2+}$, i. e. 1 mmol./l. The values of $\kappa$ at pH 11 and pH 3 may be almost equal since it is evaluated by analogy with the experimental results by Gaudin and Chang[4] that the decrease of $Ba^{2+}$ concentration in bulk solution resulting from the adsorption of $Ba^{2+}$ is of the order of 10%, which corresponds to the decrease of $\kappa$ of about 3% under the adopted condition. As illustrated in Fig. 4, the $\zeta$ potential of quartz in the solution containing $Ba^{2+}$ of 1 mmol./l. is $-11$ mV. at pH 11 and $-9$ mV. at pH 3; the value of $\zeta$ at the former where the remarkable flocculation is exhibited is somewhat higher than that at the latter where no visible flocculation is observed. From the inspection of $\kappa$ and $\zeta$, it is difficult to explain the singular flocculation in alkaline solution in terms of the decrease of repulsion in alkaline solution. These considerations will lead to the conclusion that such a flocculation in alkaline solution is not due to the decrease of the repulsion but to the incease of attraction.

The attractive potential energy should be known in addition to the repulsive potential energy in order to obtain the total potential energy of interaction between approaching particles. London-van der Waals attractive potential for two approaching flat plates has been expressed as Eq. 3[5], when $d$ is small compared with the thickness of the plates;

$$V_A = -A/48\pi d^2 \tag{3}$$

where $A$ is called "Hamaker constant". It is necessary to determine the value of $A$ in calculating $V_A$ according to Eq. 3. However, since the proper evaluation of $A$ has not yet been established, the examination by which $A$ is determined empirically has been undertaken by using Eq. 4,

$$\left.\begin{array}{l} C_{\text{floc.}} = 3.1\times10^{-24}z^4/A^2v^6 \text{ mmol./l.} \\ \qquad \text{at } 25^{\circ}\text{C} \\ z = ve\zeta/\boldsymbol{kT} \end{array}\right\} \tag{4}$$

which is derived as a flocculation value from Eqs. 2 and 3 on the basis of the Verwey-Overbeek theory. Thus, $A$ was determined to be $3.4\times10^{-13}$ *, where the empirical value of $C_{\text{floc.}}$ of $Ba^{2+}$ and $\zeta$ potential were 3 mmol./l. and $-20$ mV. respectively. In Fig. 6, the total potential energy curves at pH 11 under various

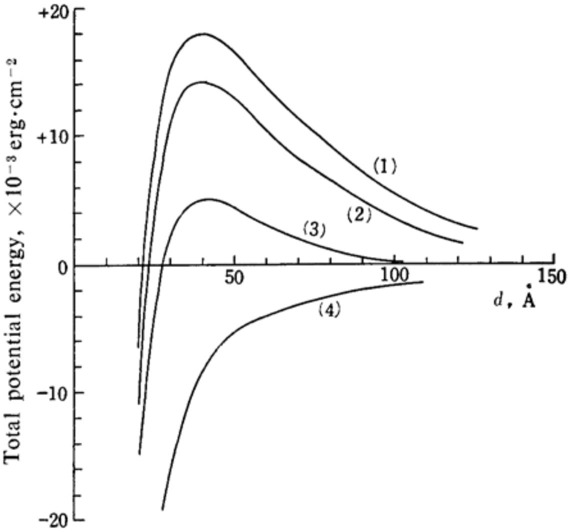

Fig. 6. Total potential energy between approaching quartz particles in solutions containing $Ba^{2+}$ at pH 11.0 as a function of half-distance of separation.

(1) $Ba^{2+}$ 0.1 mmol./l.
(2) $Ba^{2+}$ 0.2 mmol./l.
(3) $Ba^{2+}$ 0.6 mmol./l.
(4) $Ba^{2+}$ 1.0 mmol./l.

concentrations of $Ba^{2+}$, i. e. 0.1, 0.2, 0.6 and 1.0 mmol./l., are illustrated as a function of half-distance of approaching particles. It can be seen from this figure that there is a potential barrier of about $5\times10^{-3}$ erg./cm² at $Ba^{2+}$ concentration of 0.6 mmol./l. which is the flocculation value at pH 11. The barrier corresponds to 7500 $\boldsymbol{kT}$ per particle if a stably suspended quartz perticle is assumed to be a cube of 1 $\mu$ edge length, or to 75 $\boldsymbol{kT}$ if 0.1 $\mu$ edge length is assumed*; This will be an insurmountable obstacle to flocculation.

Now, the discrepancy between the flocculation experiment and the potential energy consideration may well be explained by assuming a certain attractive force by which the potential barrier is lowered. Mattson[7] has suggested that the strong flocculation of quartz particles in alkaline solution is due to the formation of particle-paricle linkage action through polyvalent cation, see Fig. 7. These linkage actions may well be supported by the consideration of energy described above. At first sight, it seems possible to explain the remarkable flocculasion of the suspention containing $Fe^{3+}$ in the range of neutral pH in terms of the

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4) A. M. Gaudin and C. S. Chang, *Min. Eng.*, **4**, 193 (1952).

5) E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids", Elsevier, Amsterdam, (1948), p. 101.

* $A$ is taken as $1\sim2\times10^{-12}$ by Verwey and Overbeek, and $\lessdot 5\times10^{-14}$ by Derjaguin[6].

6) B. V. Derjaguin, *Discussions Faraday Soc.*, **18**, 36 (1954).

* A sphere of 1.0 $\mu$ in diameter and of specific gravity 2.7 falling in water under the influence of gravity aquires a kinetic energy of only $6\times10^{-21}$ erg or of $1.5\times10^{-7}$ in unit of $\boldsymbol{kT}$.

7) S. E. Mattson, *Kolloidchem. Beihefte*, **14**, 227 (1922).

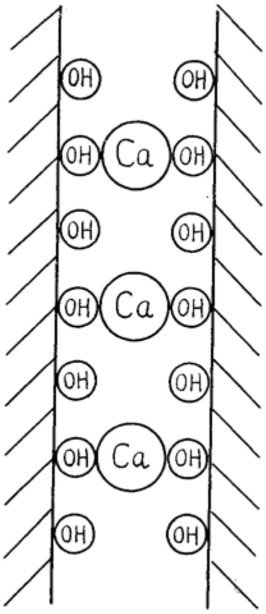

Fig. 7. Schematic illustration of linkage action of $Ca^{2+}$.

lowering of ζ potential (see Figs. 3 and 5); the value of ζ lies in zero or in its vicinity at about neutral pH. However, there is no visible flocculation of quartz particles in a solution containing $Fe^{3+}$ 0.14 mmol./l. at pH 3.5 despite the fact that the ζ potential is zero. In the case of the suspension containing $Cu^{2+}$, it is understood by the inspection of ζ potential data that the repulsive potential between particles in the pH range of 9∼11, wherein a violent flocculation takes place, is higher than that at pH 5.2 wherein no visible flocculation is observed.

Thus, the flocculation depending upon the pH of the solution containing $Fe^{3+}$ or $Cu^{2+}$, as well as the case where $Ba^{2+}$ is contained, can not be interpreted only in terms of the decrease of repulsion caused by the decrease of ζ potential. An uncertainty still remains whether these flocculation characteristics are due to the bridging action by metal ion and $OH^-$ as in the case of $Ba^{2+}$ and $OH^-$ or to the so-called "heteroflocculation"[8], between metal hydroxide and quartz perticles. The flocculation mechanism of macromolecular flocculants for suspensions has been interpreted by the concept of molecular bridging action caused by its fibrous structure[9]. It is now worthwhile to point out that, in the case where a simple metallic ion is involved, not only London-van der Waals attractive force but also a certain attractive force by which a special linkage action is brought about must be taken into account.

## Summary

The effects of pH on the flocculation of quartz aqueous suspensions containing $Ba^{2+}$, $Fe^{3+}$ or $Cu^{2+}$, respectively, were investigated by means of electrokinetic measurements. The violent flocculation takes place in the characteristic range of pH with respective cation involved. The calculation of the potential energy between approaching quartz particles indicates that the violent flocculation is readily explained, not by the decrease of electrical repulsion, but by the consideration of an attractive force other than van der Waals attraction.

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[8] B. V. Derjaguin, *Discussions Faraday Soc.*, **18**, 85 (1954).

[9] R. A. Ruehrwein and D. W. Ward, *Soil Sci.*, **73**, 485 (1952).