Original Paper

Activation with Polyvalent Metal Salts in the Anionic Flotation of Starch —Fundamental Study on the Removal of Organic Matters from Wastewater—

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Kyoto 606-8501, Japan**Abstract**

The effects of hydrolysable metal salts on the flotation of potato starch with anionic surfactant, sodium dodecylsulfate, were investigated. It was presented that negatively charged starch surface was activated by the hydrolysable metal salts of Al(III), Fe(III), Cu(II) and Ni(II). The pH range in which the activation was observed ranged from the precipitation pH of each metal hydroxide to the isoelectric point, IEP, of each hydroxide precipitate. SEM images indicated that starch particles were covered with hydroxide precipitate above the precipitation pH. The results of adsorption test and micro electrophoresis indicated that the effect of adsorbed hydroxy complex was not sufficient to reverse the negative charge of starch surface. These results suggested that in the anionic flotation of starch it was not hydroxy complexes but hydroxide precipitates that acted as an activating species which modified the starch particle surface.

Key words: Starch, Anionic flotation, Activation, Metal hydroxide, Sodium dodecyl sulfate

1. Introduction

Flotation is known as an effective unit operation in mineral processing. Recently, flotation is being practiced in other fields like recycling or environmental field such as plastics separation and recycling¹⁾, separation or harvesting of micro-organisms^{2,3)}, harvesting or removal of algae⁴⁾. However, unlike in mineral processing, the particulate product which is subject to flotation especially in environmental applications usually includes many kinds of organic substances. Compared to mineral processing field, fundamental studies have not been sufficiently done so far.

In the previous report⁵⁾ that was part of fundamental studies on the separation of organic particles in wastewater using a flotation technique, the feasibility of collecting starch particles, the test sample of organic suspended solid, into the froth product has been investigated and discussed the flotation behavior in connection with the results of the electrokinetic and adsorption measurements.

In this paper, the effect of metal salts on the flotation behavior of potato starch was investigated

in the presence of anionic collector of sodium dodecyl sulfate. In a physicochemical separation system, hydrolyzed metal cations modify the negatively charged mineral surface in a number of ways. Generally, they have been used in the flotation of oxide and sulfide minerals^{6–10)} and in liquid-liquid extraction, the role of hydrolysable metal cation having been studied^{11–12)}. Recently, they have been used in the deinking process in paper recycling for the removal of ink using flotation¹³⁾. In this investigation, particularly, the flotation test using anionic collector and metal chlorides of Al(III), Fe(III), Cu(II) and Ni(II) as activators was carried out in order to investigate the effect of these metal salts on the surface property of starch particle and floatability. Adsorption test, scanning electron microscopy and electrokinetic measurements were also carried out and the results were compared to that of flotation experiment to discuss the activating mechanism of the metal salts used.

2. Materials and methods

Reagent grade potato starch powder was used as a solid sample. Particle size distribution of the potato starch is shown in Fig. 1. Sodium dodecyl sul-

Fig. 1 Particle size distribution of potato starch.

fate (SDS) was used as collector. Aluminium (III) chloride hexahydrate, $\text{Al(III)Cl}_3 \cdot 6\text{H}_2\text{O}$, Iron (III) chloride hexahydrate, $\text{Fe(III)Cl}_3 \cdot 6\text{H}_2\text{O}$, copper (II) chloride dehydrate, $\text{Cu(II)Cl}_2 \cdot 2\text{H}_2\text{O}$ and nickel (II) chloride hexahydrate, $\text{Ni(II)Cl}_2 \cdot 6\text{H}_2\text{O}$ were used as activator. The pH of suspension was adjusted by hydrochloric acid, HCl, sodium hydroxide, NaOH, and sodium chloride, NaCl, was used as supporting electrolyte. All the materials and reagents were obtained from Nacalai Tesque Inc., Japan and used as received.

Flotation experiment was carried out using a Kyoto University-type flotation machine (450 ml of cell capacity) with a central stirrer and bubble supply. Suspension was prepared as follows. A given concentration of starch particle was suspended. After pH regulation, a given amount of solution which contained a certain concentration of metal salt was added into the suspension. The suspension stood for 10 min at room temperature. Successively, a given amount of solution which contained a certain concentration of SDS was added into the suspension. The suspension stood again for 10 min at room temperature. After that, flotation was carried out for 2 min and floated starch particles were collected, filtered and dried in vacuum before weighing. The pH of the suspension was measured after flotation.

Adsorption test was carried out with following procedure. A given amount of potato starch particles was dispersed into distilled water and degassed in vacuum for 3 min. After degassing, the pH of the suspension was adjusted and a given amount of solution which contained a certain concentration of metal salt was added into the suspension. Successively, the suspension was put into

thermostatic bath and shaken with shaking apparatus at 298 K. After a given time, the suspension was subject to pH measurement and to filtering using a membrane filter. The residual concentration of metal species in the filtrate was measured by ICP spectrophotometer, ICAP-575 II (Nippon Jarrel Ash Co., Japan) and the amount of adsorption was determined.

The surface morphology of starch particle was investigated with scanning electron microscope, S-3500H (Hitachi, Japan) after 10 min contact with solution containing 0.1 mol dm^{-3} metal cation at a given pH. The suspension was prepared as the same way as described in adsorption experimental section. Starch particles was filtered and washed with distilled water and dried in vacuum at room temperature. The presence of metal species on starch particles was confirmed with EPMA measurement.

The electrophoretic mobility of the potato starch particle and hydroxide precipitate of Al(III) were measured by microelectrophoresis. Suspension was prepared as the same way as adsorption experiment, but ionic concentrations of the suspensions for the measurement of starch particle without Al(III) and the suspension of hydroxide precipitate were adjusted by NaCl to constant ($6 \times 10^{-3} \text{ mol dm}^{-3}$). The pH was measured after the electrophoresis measurement.

The hydroxide precipitate of Al(III) was prepared by neutralizing the solution containing a certain concentration of metal salt with sodium hydroxide. The precipitates were filtered, washed with distilled water and dried in vacuum at room temperature.

3. Results and discussion

Floatability of the starch particle in the presence of $10^{-4} \text{ mol dm}^{-3}$ SDS at two different levels of the metal salt, 0 and $10^{-3} \text{ mol dm}^{-3}$, is shown in Figs. 2 to 5. As can be seen from these figures, the starch particles do not float without the metal salts throughout the investigated pH range. It has been suggested that dodecyl sulfate anions, DS^- , does not adsorb onto the starch particle surfaces due to the electrostatic repulsion between the negatively charged starch surface and DS^- (see Fig. 12). In the presence of a metal salt, on the other hands, the floatability increases with increasing pH over a certain pH value, pH 5.4 for Al(III), pH 2.9 for Fe(III), pH 6.1 for Cu(II), and pH 7.4 for Ni(II), and reaches the maximum value of almost 100%. The floatability suddenly decreases with increasing pH over a certain pH, 7.2 for Al(III), 7.1 for

Fig. 2 Floatability of potato starch with 10^{-3} mol dm $^{-3}$ sodium dodecyl sulfate as a function of pH in the absence and presence of 10^{-3} mol dm $^{-3}$ Al $^{3+}$.

Fig. 4 Floatability of potato starch with 10^{-3} mol dm $^{-3}$ sodium dodecyl sulfate as a function of pH in the absence and presence of 10^{-3} mol dm $^{-3}$ Cu $^{2+}$.

Fig. 3 Floatability of potato starch with 10^{-3} mol dm $^{-3}$ sodium dodecyl sulfate as a function of pH in the absence and presence of 10^{-3} mol dm $^{-3}$ Fe $^{3+}$.

Fig. 5 Floatability of potato starch with 10^{-3} mol dm $^{-3}$ sodium dodecyl sulfate as a function of pH in the absence and presence of 10^{-3} mol dm $^{-3}$ Ni $^{2+}$.

Fe(III), and 7.7 for Cu(II), whereas it keeps around 100% in the system including Ni(II).

In order to know the physicochemical aspect of the activation mechanism by the metal salt in the SDS-starch system, the concentration of the metal species in the condition similar to the flotation test was calculated.

In Figs. 6 to 9, the species distribution diagrams for 10^{-3} mol dm $^{-3}$ of each aqueous metal species are presented as a function of aqueous pH. Calculations were performed using the equilibrium constants¹⁴⁾ tabulated in Table 1. As shown in Figs. 6 to 9, aluminum(III) hydroxide precipitates at pH 4.1, iron(III) hydroxide at pH 1.8, copper(II) hydroxide at pH 5.9, and nickel(II) hydroxide at pH 8.2. These diagrams give us outline for realiz-

ing the flotation results by considering which specie is predominant in a certain pH range. Comparing each result of flotation and each diagram shows that all the activation ranges observed in this study are within the pH ranges in which each hydroxide precipitate is predominant. In general, activation arises from the pH ranges in which hydroxy complex is formed prior to hydroxide precipitation in a number of publications⁶⁻¹²⁾. However, such activation pattern is not observed in this study. This difference suggests that hydroxy complex do not contribute to the activation of the starch particle while hydroxide precipitates play an important role as activator in this system. In the following sections, the effects of the formation of hydroxy complex and that of the hydroxide pre-

Table 1 Hydrolysis for Al(III), Fe(III), Cu(II), Ni(II) and their overall stability constants, $K^{14)}$.

Reactions	log K
$\text{Al}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{AlOH}^{2+} + \text{H}^+$	-5.4
$\text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_2^+ + 2\text{H}^+$	-9.98
$\text{Al}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_3(\text{aq}) + 3\text{H}^+$	-15.7
$\text{Al}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_4^- + 4\text{H}^+$	-23.6
$2\text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}_2(\text{OH})_2^{4+} + 2\text{H}^+$	-7.7
$3\text{Al}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Al}_3(\text{OH})_4^{5+} + 4\text{H}^+$	-13.7
$\text{Al}(\text{OH})_3(\text{s}) + 3\text{H}^+ \rightleftharpoons \text{Al}^{3+} + 3\text{H}_2\text{O}$	9.2
$\text{Fe}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{FeOH}^{2+} + \text{H}^+$	-2.56
$\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2^+ + 2\text{H}^+$	-6.19
$\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3(\text{aq}) + 3\text{H}^+$	-10
$\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_4^- + 4\text{H}^+$	-21.9
$2\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2(\text{OH})_2^{4+} + 2\text{H}^+$	-2.85
$3\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3(\text{OH})_4^{5+} + 4\text{H}^+$	-6.1
$\text{Fe}(\text{OH})_3(\text{s}) + 3\text{H}^+ \rightleftharpoons \text{Fe}^{3+} + 3\text{H}_2\text{O}$	2.5
$\text{Cu}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CuOH}^+ + \text{H}^+$	-8.2
$\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_2(\text{aq}) + 2\text{H}^+$	-17.5
$\text{Cu}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_3^- + 3\text{H}^+$	-27.8
$\text{Cu}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_4^{2-} + 4\text{H}^+$	-39.1
$2\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}_2(\text{OH})_2^{2+} + 2\text{H}^+$	-10.6
$\text{Cu}(\text{OH})_2(\text{s}) + 2\text{H}^+ \rightleftharpoons \text{Cu}^{2+} + 2\text{H}_2\text{O}$	8.85
$\text{Ni}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{NiOH}^+ + \text{H}^+$	-10.2
$\text{Ni}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Ni}(\text{OH})_2(\text{aq}) + 2\text{H}^+$	-19.2
$\text{Ni}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Ni}(\text{OH})_3^- + 3\text{H}^+$	-30
$\text{Ni}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Ni}(\text{OH})_4^{2-} + 4\text{H}^+$	-44
$2\text{Ni}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Ni}_2(\text{OH})_2^{2+} + 2\text{H}^+$	-10.5
$4\text{Ni}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Ni}_4(\text{OH})_4^{4+} + 4\text{H}^+$	-27.3
$\text{Ni}(\text{OH})_2(\text{s}) + 2\text{H}^+ \rightleftharpoons \text{Ni}^{2+} + 2\text{H}_2\text{O}$	13.3

cipitate on the floatability of the starch particles were examined particularly in the system containing Al(III) species.

Fig. 10 shows the adsorption isotherm of Al(III) species onto the starch particle surface. The pH was 3.7 ± 0.2 and the conditioning time was 10 min. As can be seen from Fig. 10, Al(III) species shows the Langmuir-type adsorption onto the starch particle surface at this pH as is the case with adsorption onto oxide minerals.

In Fig. 11, the adsorption of Al(III) species onto the starch particle is presented as a function of pH. The adsorption occurs in the pH range in which hydroxy complex is formed as shown in Fig. 6. As in Fig. 2, however, flotation activation is not observed in this pH range. Electrophoresis data indicate us one of the reasons why activation does not occur.

The electrophoretic mobility of the starch with $10^{-3} \text{ mol dm}^{-3}$ Al(III) is shown in Fig. 12. As can be seen from Fig. 12, The mobility is positively

Fig. 6 Species distribution diagram for $10^{-3} \text{ mol dm}^{-3}$ Al(III). **Fig. 7** Species distribution diagram for $10^{-3} \text{ mol dm}^{-3}$ Fe(III). **Fig. 8** Species distribution diagram for $10^{-3} \text{ mol dm}^{-3}$ Cu(II).

Fig. 9 Species distribution diagram for $10^{-3} \text{ mol dm}^{-3}$ Ni(II).

Fig. 10 Adsorption isotherm of Al(III) species onto starch at $\text{pH } 3.7 \pm 0.2$.

shifted from the values without Al(III). The difference between the mobility with and without the Al(III) salt increases with increasing pH from 2.7 to 4.0. This coincides with increasing amount of adsorbed Al(III) as shown in Fig. 11. These results indicate that the adsorption of hydroxy complex of Al(III) onto the starch surface is not effective to reverse the surface charge of starch particle. This might be the reason why activation is not observed in each pH range in which each hydroxy complex formed. This might be attributed to nano-sized pore which was observed on starch surface^{15, 16}. The absorption of hydroxy complex seems to occur not only on the starch surface but also inside the starch particle. Consequently, the effect of hydroxy complex on the surface charge is weakened. However, further detailed investigation should be needed.

Fig. 11 Amount of Al(III) species adsorbed on starch as a function of pH.

Fig. 12 Electrophoretic mobility of starch particle and Al(OH)_3 precipitate as a function of pH.

So as to the effect of hydroxide precipitate on the flotation of starch, as described above, all the activation pH ranges observed in this investigation are almost within the pH ranges in which each hydroxide precipitate is predominant as shown in the species distribution diagrams. It seems to be important to observe the adhesion of hydroxide precipitate onto the starch particle and to correlate it with the activation of starch flotation.

In Fig. 13, the SEM images of the starch particles are presented. As can be seen from Fig. 13(a), any incrustation is not observed on the starch particle surface below the precipitation pH. Above the precipitation pH, on the other hand, it is observed that the starch particle surface is covered with hydroxide precipitate (Figs. 13(b) and 13(c)). In consequence, the surface property of the starch particle above the precipitation pH is almost the

Fig. 13 SEM images of starch treated with 0.1 mol dm^{-3} Al(III) solution (a) below the precipitation pH, (b) over the precipitation pH, and (c) over the PZC of Al(OH)_3 precipitate. Conditioning time is 10 min at 25°C .

same as that of the respective hydroxide precipitate, and therefore, the increase in floatability can be explained by the adsorption of DS^- onto the starch particle covered with the hydroxide precipitate. Actually the electrophoresis data of the hydroxide precipitate, which is presented in Fig. 12, shows that it is positively charged below its isoelectric point, IEP, and negatively charged above the IEP. Probably, DS^- adsorbs onto the positively charged hydroxide precipitate coating on the starch particle by electrostatic interaction. Moreover, as shown in Fig. 2, the activation is diminished when the pH increases above the IEP of the precipitate. From these results, the disappearance of activation could be explained by the diminishing of electrostatic attraction between DS^- and hydroxide precipitate on starch particle.

In Table 2, the calculated precipitation pH of metal hydroxide, the IEP of precipitate^{17, 18)}, and the pH range in which 80% floatability of starch in the presence of $10^{-3} \text{ mol dm}^{-3}$ metal salt is observed in this investigation are tabulated. Comparing these values, the activation pH range observed in this investigation is within the pH range between the precipitation pH and the IEP of hydroxide precipitate. From these results, it might be concluded that the electrostatic interaction between DS^- and hydroxide precipitate coating on the starch surface is one of the important factors for the activation of starch particle.

4. Conclusion

In this study, the effect of hydrolysable metal salts on the surface property of starch particle and its floatability was investigated. The results obtained are summarized as follows.

- (1) Negatively charged starch surface was activated by adding hydrolysable metal salts of Al(III), Fe(III), Cu(II), and Ni(II). The pH range in which the activation in flotation was observed ranged from the precipitation pH to the IEP of each metal hydroxide.
- (2) From the results of adsorption experiment and electrokinetic measurement, it was pointed out

Table 2 Precipitation pH, PZC of hydroxide precipitates and the activation area observed in the flotation test. (*G.A. Parks: Chem. Rev., 65, 2, pp.177–198 (1965); **Previous work)

Precipitate	Precipitation pH	PZC of precipitate	Activation area
Al(OH)_3	4.1	9.5 (this work)	5.6–9.4
Fe(OH)_3	1.8	7–8*	3.6–8.0
Cu(OH)_2	5.9	10–11**	7.0–9.2
Ni(OH)_2	8.2	>12**	8.4–11.6

that the adsorption of metal hydroxy complex onto starch surface did not give sufficient effect to reverse the negative surface charge of starch particle.

- (3) SEM images showed that starch surface was covered with hydroxide precipitate above the precipitation pH. It was suggested that hydroxide precipitate played an important role in activation in the flotation of starch.
- (4) From these result obtained above, it was suggested that metal-hydroxy complex does not act as an activating species in the anionic flotation of starch, unlike in that of oxide or sulfide minerals, whereas hydroxide precipitate act as an activating species with which the starch particle surface is covered. It was also confirmed by the adsorption, electrophoretic, and SEM measurements that the surface property of starch particle was modified by coating its surface with metal hydroxide and that activation disappeared due to decrease in surface charge of precipitate toward negative value above the IEP of precipitate.

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