Studies of the Removal of Cd^{2+} Ions by Adsorbing Particle Flotation

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The conditions for the removal of Cd^{2+} ions from an aqueous solution by adsorbing particle flotation using bentonite and a cationic surfactant has been investigated. It has been found that the most suitable method was to conduct flotation in the region of the coagulation flotation of bentonite. The addition of polyacrylamide (PAA) extended not only the region of coagulation flotation towards lower and higher hexadecyltrimethylammonium chloride (HTAC) concentrations tested, but also increased the flotation efficiency (expressed as the percentage of ions removed from the total solution). The selective flotation from an aqueous solution containing two kinds of metal ions was also investigated. Each metal ion could be floated from the solution with the pH of the metal hydroxide formation. By selecting proper conditions, it was possible to remove each metal ion separately from a mixed solution.

It has been well-known that the suspended particles in an aqueous solution are coagulated and precipitated by the addition of coagulating agents.[1-5] On the other hand, the suspended particles in an aqueous solution can be floated by adhering them on bubbles by the addition of collectors or foaming agents.[6-10] It is also known that the surfactant changes the state of suspension of the particles, from coagulation precipitation through coagulation flotation to redispersion, with an increase in the amount of surfactant added.[11,14]

Since ions in solution are adsorbed on bentonite as an ion-exchanger, the flotation of bentonite is considered to have a close relation to the removal of ions. Such an ion flotation is called "adsorbing particle flotation."[11] Adsorbing particle flotation is perhaps one of the most effective methods for the ion flotation. The method consists of a simple adsorption or exchange adsorption of ions from a solution onto adsorbent particles like bentonite, which are subsequently floated by the addition of a suitable surfactant.[12]

The present paper will describe a study of the phenomena of the coagulation flotation of bentonite suspensions and the adsorbing particle flotation of Cd^{2+} ions and a Cd^{2+}–Cu^{2+} ion mixture by the addition of bentonite. The explanation of the mechanism of such an ion flotation will also be attempted.

Experimental

Materials. The bentonite powder (Bt) used as an ion-exchanger was obtained from the Wako Pure Chemical Co., Ltd.; the fraction passing through a 350-mesh sieve was collected and dried under reduced pressure. The pure-grade hexadecyltrimethylammonium chloride used as a cationic surfactant, obtained from the Kao Soap Co., Ltd., was used without further purification. A stock solution containing 1.78×10^{-4} mol/l cadmium ions (Cd^{2+}) was prepared by dissolving Cd metal of a 99.999% purity, kindly supplied by the Laboratory of General Chemistry of our department, in nitric acid. The pH of the solution was 2.7. The cupric sulfate used was a reagent-grade $CuSO_4\cdot5H_2O$, which had been recrystallized from distilled water, a stock solution of 1×10^{-3} mol/l concentration was prepared. A stock solution containing 9.3×10^{-4} mol/l ferric ions was prepared from reagent-grade ferric chloride dissolved in triply distilled water. The polyacrylamide (PAA) with an amide content of 87% used as a coagulating agent was the product of the Nitto Chemical Co., Ltd.; it was dried under reduced pressure. Special-grade sodium hydroxide and sulfuric acid supplied by the Wako Pure Chemical Co., Ltd., were used to adjust the pH.

The water used was obtained by first refluxing ordinary distilled water with an acid permanganate solution; then it was distilled from an alkaline permanganate solution and finally distilled twice with a Hysil flask.

Apparatus and Procedure. The apparatus and method used for flotation measurements were the same as have been described.[13] Nitrogen gas humidified with water vapor and controlled to a constant rate of gas flow was bubbled through a glass filter (No. 4) into a flotation cell containing 10 ml of the sample solution. The gas-flow rate and time were kept at 10 ml/min and 7 min respectively. For the measurement of the effect of HTAC on the state of Bt suspension, a 10-ml portion of a suspension containing varying amounts of Bt and HTAC was introduced into a ground test tube 1.0 cm in inner diameter and 20.0 cm in length. The tube was then shaken, and the coagulation-dispersion and precipitation-flotation behavior was judged by the naked eye.[14] The centrifugation was applied when necessary for 20 min at 3500 rpm. The concentrations of Cu^{2+} ions, Fe^{3+} ions, and Cd^{2+} ions were measured by using an atomic absorption spectrometer (Techtron Pty., Ltd., Model-AA-100). The absorbance was measured at 3248 Å for Cu^{2+} ions, 2483 Å for Fe^{3+} ions, and 2288 Å for Cd^{2+} ions. The measurements were carried out at room temperature (about 25 °C).

The flotation efficiency of Cd^{2+}, Fe^{3+}, and Cu^{2+} ions is conventionally expressed by:

$$F = (1 - C_f/C_i) \times 100\,\%$$

where C_i and C_f are the concentrations of ions before and after the flotation.

All the experiments were run under the conditions of bubble flotation, that is, flotation using only ascending bubbles, without the aid of foam formation. Since most of the solution after flotation was used for the measurement of C_f, the flotation efficiencies calculated substantially express the percentages of these ions removed from the total solution.

Results and Discussion

Change in the Dispersion State of Bentonite upon the Addition of HTAC. Figure 1 shows the various regions of the state of bentonite after shaking as a function of the bentonite and HTAC concentrations. As may be seen, the bentonite in an aqueous HTAC solution shows the regions of dispersion, coagulation flotation, coagulation precipitation, and redispersion, as has been reported

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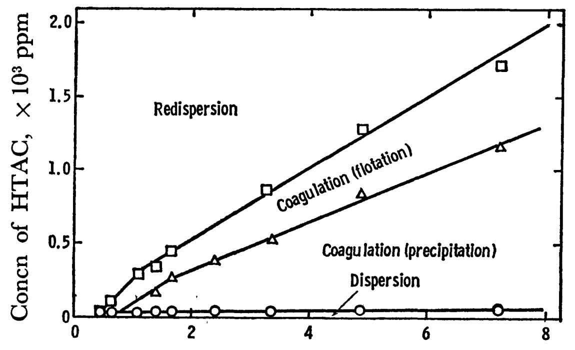

Fig. 1. Effect of HTAC on dispersion state of bentonite suspension.

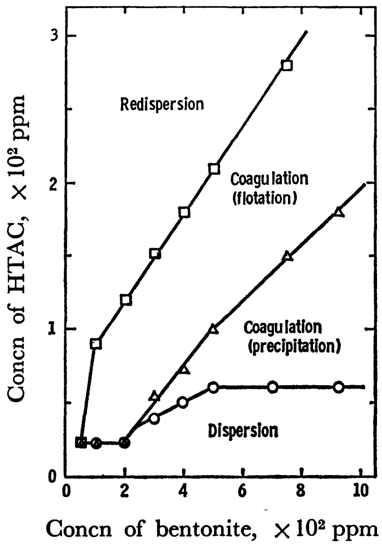

Fig. 2. Effect of HTAC on dispersion state of bentonite suspension at low concentration region.

previously.[14] In the regions of dispersion, coagulation flotation, and coagulation precipitation of Fig. 1, the layer scarecely forms on a solution, but in the region of redispersion, the stable foam layer forms with an increase in the HTAC concentration. Further, the regions of dispersion and coagulation precipitation give an opaque solution, while the region of coagulation flotation is transparent as a whole. Thus, the region of coagulation flotation seems to offer optimum conditions for bubble flotation. Also, it is noticeable that the change from coagulation precipitation to coagulation flotation is sensitive to a slight change in the HTAC concentration. Figure 2 shows the coagulation flotation region for low concentrations of Bt and HTAC especially measured in detail, which is useful for the adsorbing particle flotation.

A similar experiments was done with the addition of 10 ppm PAA as a coagulating agent. The results are shown in Fig. 3. As can be seen, the region of coagulation flotation in the Bt–HTAC–PAA system is broader with respect to the HTAC concentration and shifts towards lower concentrations with respect to the Bt concentration, compared with the Bt–HTAC system shown in Fig. 2. Therefore, the former system is more favorable for adsorbing-particle flotation than the latter.

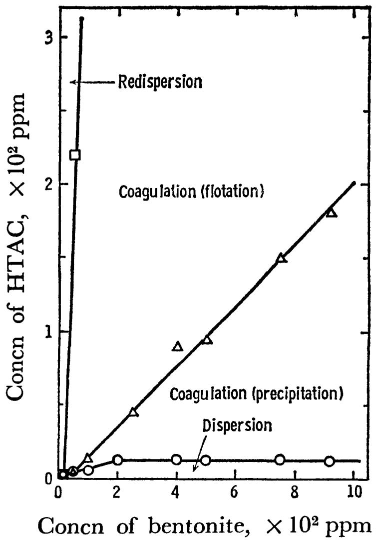

Fig. 3. Effect of HTAC on dispersion state of bentonite suspension in the presence of 10 ppm PAA.

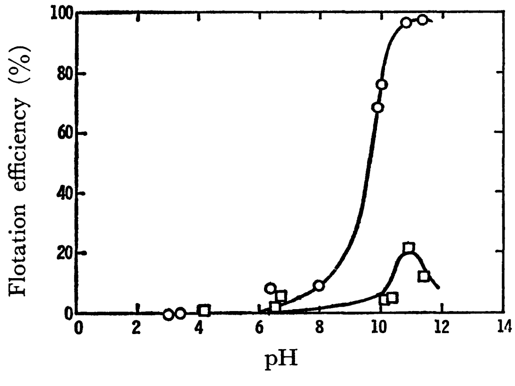

Fig. 4. Flotation rate *vs.* pH for the Cd^{2+}-Bt-HTAC system.

Cd^{2+}: 1.78×10^{-5} mol/l, HTAC: 56.8 ppm, Bt: 600 ppm (□), 100 ppm (○).

Flotation of Cd^{2+} Ions by HTAC. The adsorbing-particle flotation of Cd^{2+} was carried out under the conditions of coagulation flotation described above. The flotation was carried out for a solution containing 1.78×10^{-5} mol/l Cd^{2+}, 56.8 ppm HTAC, and 100 ppm Bt (belonging to the coagulation-flotation region) or 600 ppm bentonite (belonging to the dispersion region) under a gas flow of 7 min and a gas-flow rate of 10 ml/min. The results are shown in Fig. 4. In the case of Cd^{2+} ion flotation by 100 ppm bentonite, the flotation efficiency begins to increase at about pH 8 and a maximum F of 98% is obtained at about pH 11.3, but in the case of Cd^{2+} ion flotation by 600 ppm bentonite, the flotation efficiency is extremely low, showing a maximum of about 20% of F. In the former case, the Cd^{2+} ions are considered to float by HTAC through the bridge of bentonite, while in the latter case, the decrease in flotation efficiency may be due to the surfactants being insufficient to float the bentonite, though Cd^{2+} ions are adsorbed on the particles.

Figure 5 shows the flotation efficiency *vs.* surfactant concentration curve at an optimum pH of 11.2. The optimum efficiency of flotation was observed in the

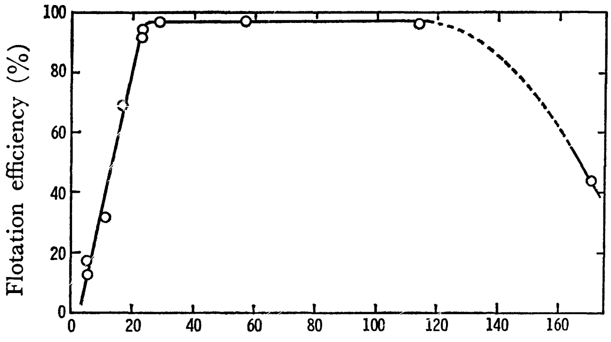

Fig. 5. Flotation rate *vs.* concentration of HTAC for the Cd^{2+}-Bt-HTAC system.
Cd^{2+}: 1.78×10^{-5} mol/l, Bt: 100 ppm, pH: 11.2.

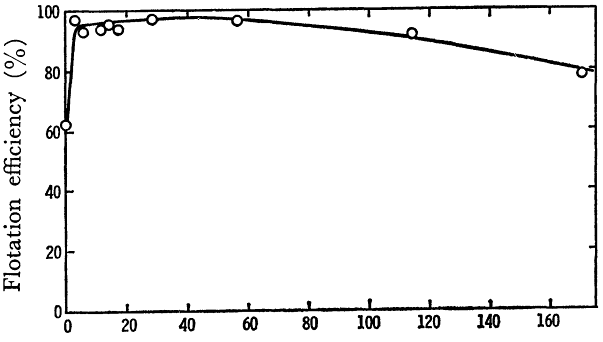

Fig. 7. Flotation rate *vs.* concentration of HTAC for the Cd^{2+}-Bt-HTAC-PAA system.
Cd^{2+}: 1.78×10^{-5} mol/l, Bt: 100 ppm, PAA: 10 ppm, pH: 11.2.

region of HTAC concentrations from about 25 to 110 ppm. It can be seen from Fig. 2 that these ranges of the HTAC concentration coincide with those of coagulation flotation. Thus, the optimum conditions for adsorbing-particle flotation are confirmed to be the region of the optimum coagulation flotation.

Flotation of Cd^{2+} Ions by HTAC and PAA. In order to study the effect of PAA, the flotation was carried out for solutions containing 1.78×10^{-5} mol/l Cd^{2+}, 100 ppm Bt, 56.8 ppm HTAC, and 10 ppm PAA under the condition of a gas-flow time of 7 min. The results are shown in Fig. 6. A comparison of Fig. 6 with Fig. 4 shows no effect of PAA addition at the optimum Cd^{2+}-Bt-HTAC composition. Then the flotation was carried out with varying concentrations of HTAC, the other conditions being kept constant at the values mentioned above. The results are shown in Fig. 7. As may be seen, the flotation efficiency remains constant down to a lower HTAC concentration than that for the system without PAA shown in Fig. 5. Above 110 ppm HTAC, the flotation efficiency sharply decreases in the case of the system without PAA, while in the case of the system with PAA, the flotation efficiency gradually decreases with an increase in the HTAC concentration above 110 ppm. Thus, the addition of PAA increases the optimum region of Cd^{2+} ion flotation towards both the lower and higher concentrations of HTAC. This increase in the region just corresponds to the increase in the region of coagulation flotation of Fig. 3 compared with that of Fig. 2. The reduction of minimum amount of 26 ppm HTAC required for the optimum flotation in the Bt–HTAC system to 3 ppm by the addition of 10 ppm PAA is particularly noticeable.

Removal of Cd^{2+} Ions by Centrifugation. To study the effects of the pH and additives on the adsorption of Cd^{2+} ions, a Bt suspension containing Cd^{2+} ions in the state of equilibrium adsorption was centrifuged and the concentration of Cd^{2+} was determined. The amount of Cd^{2+} adsorbed on Bt or the amount centrifuged was expressed by $R=(1-C_f/C_i)\times100$, which is plotted against the pH in Fig. 8. The centrifugation of Cd^{2+} ions was performed for 20 min at 3500 rpm for the Cd^{2+}–Bt–HTAC–PAA (A), Cd^{2+}–Bt–HTAC (B) and Cd^{2+}–Bt (C) systems with the compositions shown in Fig. 8. In the cases of A and B, the efficiency of the centrifugation of Cd^{2+} ions begins to increase rapidly at about pH 8 and a maximum of $R=98\%$ was obtained. In the case of C, the value of R stays rather high in the low pH region and begins to increase at pH 8, but the maximum is only 79%, attained at pH 11.3.

These facts confirm that, at an optimum pH of 11.3, the adsorption of Cd^{2+} is complete in A, B, and C, but

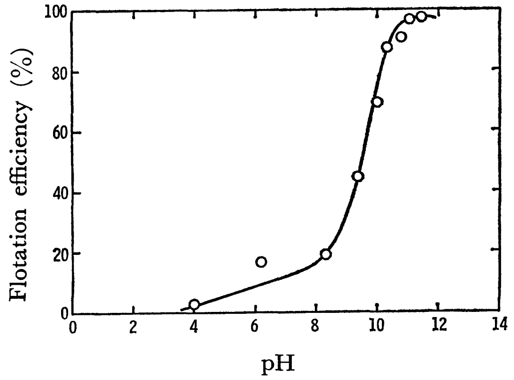

Fig. 6. Flotation rate *vs.* pH for the Cd^{2+}-Bt-HTAC-PAA system.
Cd^{2+}: 1.78×10^{-5} mol/l, Bt: 100 ppm, HTAC; 56.8 ppm, PAA: 10 ppm,

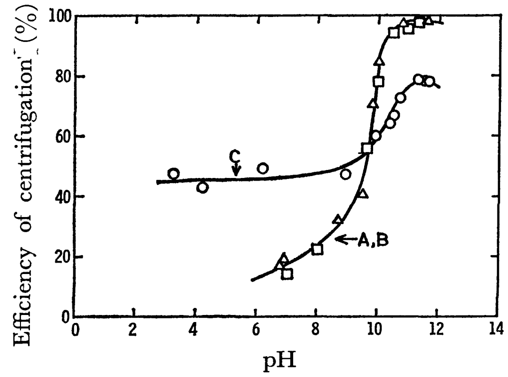

Fig. 8. Effect of pH on rate of Cd^{2+} adsorption on Bt.
Cd^{2+}: 1.78×10^{-5} mol/l, A: 100 ppm Bt, 56.8 ppm HTAC, 10 ppm PAA, B: 100 ppm Bt, 56.8 ppm HTAC, C: 100 ppm Bt.

the aggregates do not grow sufficiently large in the case of C to be centrifuged completely during 20 min, as is the case in A and B, while the removal of rather large amounts of Cd^{2+} in the pH region for C is due to a certain amount of Bt being centrifuged, upon which some Cd^{2+} ions are adsorbed, not hindered by the adsorption of HTAC which may occur in the cases of A and B. At any rate, it is confirmed that, in the cases of A and B, Cd^{2+} ion flotation is realized by the ions being adsorbed on Bt particles, which are subsequently coagulated and floated by bubbles.

Selective Ion Flotation from a Mixed System. The flotation of Cd^{2+} and Cu^{2+} ions from a solution containing 1.78×10^{-5} mol/l Cd^{2+} ions, 1×10^{-4} mol/l Cu^{2+} ions, 100 ppm Bt, and 56.8 ppm HTAC under the condition of a gas-flow rate of 10 ml/min was carried out while varying the pH. The results are shown in Fig. 9. In the mixed system, Cd^{2+} and Cu^{2+} ions are floated above pH 6 and 8 respectively, much as in the flotation of the separate system.[13] Thus, even in the mixed system the flotation begins from the point of the formation of insoluble cadmium and copper hydroxide. According to this finding, Cu^{2+} ions are exclusively floated between pH 6 and 8 and it is possible to separate Cu^{2+} ions from the mixed system by the control of the pH. From the color of the scum, it is clear that copper hydroxide has formed.

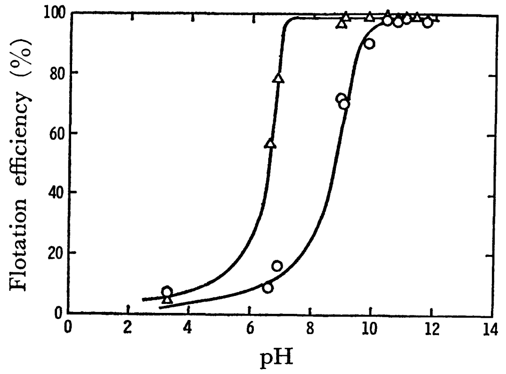

Fig. 9. Selective flotation of Cd^{2+} and Cu^{2+} ions.
Cd^{2+}: 1.78×10^{-5} mol/l (○), Cu^{2+}: 1×10^{-4} mol/l (△), Bt: 100 ppm, HTAC: 56.8 ppm.

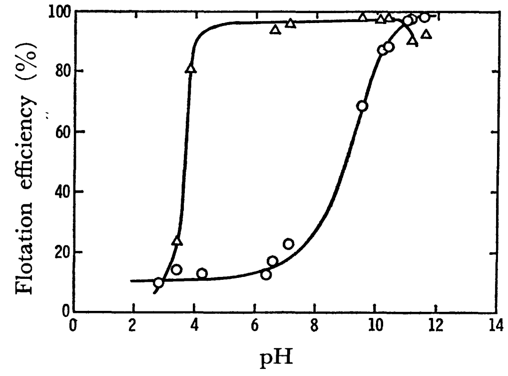

Fig. 10. Selective flotation of Cd^{2+} and Fe^{3+} ions.
Cd^{2+}: 1.78×10^{-5} mol/l (○), Fe^{3+}: 4.65×10^{-5} mol/l (△), Bt: 100 ppm, HTAC: 56.8 ppm.

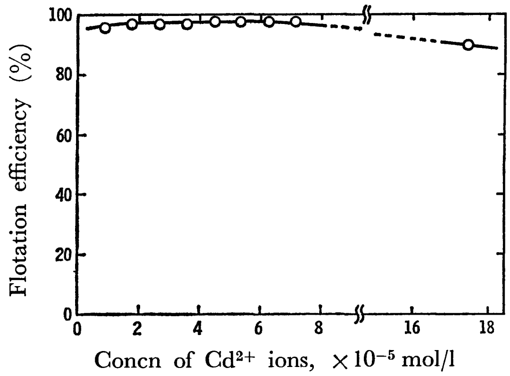

Fig. 11. Flotation rate *vs.* concentration of Cd^{2+} ions for the Cd^{2+}-Bt-HTAC system.
Bt: 100 ppm, HTAC: 56.8 ppm, pH: 11.4.

Figure 10 shows the results of the flotation of Cd^{2+} and Fe^{3+} ions from a solution containing 1.78×10^{-5} mol/l Cd^{2+} ions, 4.65×10^{-5} mol/l Fe^{3+} ions, 100 ppm Bt, and 56.8 ppm HTAC. Beyond pH 10, the complete flotation of both Cd^{2+} and Cu^{2+} is possible, showing about a 98% of flotation efficiency for both ions. In this system, as in the Cd^{2+} and Cu^{2+} systems, Fe^{3+} and Cd^{2+} ions are floated from the respective pH of the insoluble hydroxide formation, and selective flotation is possible by the method of a starvation dose, [15] although about 10% of the Cd^{2+} ions are floated even in the pH region of less than 8, which is not the case for the system containing Cd^{2+} ions alone, as is shown in Fig. 4. This may be due to some Cd^{2+} ions being adsorbed together with Fe^{3+} ions on the Bt particles. The phenomenon is preferably called coadsorption. In the case of limited amounts of cationic surfactant and Bt, it may be expected that, as the flotation of Cd^{2+} ions begins to occur above pH 8, the flotation efficiency of Fe^{3+} ions will gradually decrease with an increase in the pH above pH 10.7.

Effect of the Cd^{2+} Ion Concentration on the Flotation Efficiency. Under the optimum conditions of 100 ppm Bt, 56.8 ppm HTAC, and pH 11.5, the effect of the concentration of Cd^{2+} ions on the flotation efficiency was studied. The results are shown in Fig. 11. As may be seen, in the Cd^{2+} concentration region from about 1×10^{-5} to 7×10^{-5} mol/l, the optimum flotation efficiency of $F=98\%$ was obtained. In the more concentrated solution of 1.78×10^{-4} mol/l, the flotation efficiency decreases to about $F=90\%$. The optimum concentration of the order of magnitude of 10^{-5} mol/l is in agreement with the conditions under which ion flotation is usually carried out.

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