The Effects of Anionic and Cationic Surfactants on the Ion Flotation of Cd^{2+}

Koichi KOBAYASHI*

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo 158

(Received November 16, 1974)

The ion flotation of Cd^{2+} ions has been investigated from the surface chemical point of view in comparison with the case of Cu^{2+} ions reported previously.[1] The effects of the change in the pH, the anionic and cationic surfactants, and bentonite on the flotation rate have also been studied. Sodium α-sulfolaurate proved to be one of the best surfactants among the anionic surfactants used for removing Cd^{2+} ions, showing as high as a 97% removal. About 97% of the Cd^{2+} ions could be floated in the region of pH 11.3 when a cationic surfactant was used with bentonite, regardless of the exact surfactant used. The addition of bentonite reduced the foam formation and liquid hold-up, resulting in effective bubble flotation. This behavior was as a whole similar to that of Cu^{2+} ions.[1] However, in all the flotation systems tested, the flotation rate increased sharply at about pH 8, and the flotation rate *vs.* pH curve for Cd^{2+} shifted towards a more alkaline region than that for Cu^{2+}, because of the stronger basic nature of the former. Also, the flotation rate of Cd^{2+} ions for the Cd^{2+}-anionic surfactant systems attained a steady value after about 7 min, longer than the 2-min gas flow required in the case of Cu^{2+} ion flotation. The adjustment of the pH using ammonia gave a lower rate of flotation than in the case of flotation using sodium hydroxide.

The importance of the process of ion flotation[2,3] is well known, as has already been mentioned in a previous paper reporting the bubble flotation of Cu^{2+} ions.[1]

The flotation of Cd^{2+} ions has become an important problem in connection with water pollution and sewage treatment.[4–6] As regards the flotation of Cd^{2+} ions, however, only a limited number of papers have been reported. Ferguson *et al.* have reported the removal of CdS using hexadecyltrimethylammonium bromide.[7] Shimoiizaka *et al.* have studied the removal of Cd^{2+} ions from mine water by using xanthates.[5] Also, this problem is of surface chemical interest, since Cd^{2+} ions are a stronger base and are fairly different chemically compared with the Cu^{2+} ions previously studied.

The present paper will report a study of the bubble flotation of cadmium ions by anionic and cationic surfactants with bentonite in order to find the condition of most efficient ion flotation, to make clear the mechanism of flotation, and to compare it with the case of Cu^{2+} ion flotation.

Experimental

Materials. A stock solution containing 1.78×10^{-4} mol/l cadmium ions (Cd^{2+}) and with a pH of 2.7 was prepared by dissolving Cd metal of a 99.999% purity (obtained from the Wako Pure Chemical Co., Ltd.) in nitric acid. The surfactants used were sodium *n*-dodecylsulfate (SDS), sodium laurate (LNa), sodium *n*-dodecylbenzenesulfate (DBS), and sodium α-sulfolaurate (α-SLNa) (obtained from the Kao Soap Co., Ltd.) as anionic surfactants, and *n*-dodecyltrimethylammonium chloride (DTAC) (obtained from the Tokyo Kasei Industrial Co., Ltd.), hexadecyltrimethylammonium chloride (HTAC) and octadecyldimethylbenzylammonium chloride (OBAC) (obtained from the Kao Soap Co., Ltd.) as cationic surfactants. The bentonite powder used as an ion exchanger was obtained from the Wako Pure Chemical Co., Ltd. The methods of the purification of the materials were the same as have previously been described[1] except for the case of OBAC. The commercial product of OBAC was recrystallized twice from acetone. The surfactants were kept in a desiccator. The pH of the solution was controlled by using special-grade sodium hydroxide and ammonia.

The triply distilled water used was free from Cd^{2+} ions, as detected by means of an atomic absorption spectrometer.

Apparatus and Procedure. The flotation apparatus and method were the same as those described previously.[1] Nitrogen gas humidified with water vapor and controlled to a constant rate of gas flowing was bubbled through a glass filter of No. 4 into a flotation cell containing 10 ml of the sample solution.

To prepare a sample solution of Cd^{2+} ions, 2 ml of the stock solution of Cd^{2+} ions, a proper amount of sodium hydroxide or ammonia to adjust the pH, 2 ml of the surfactant solution, and 2 ml of bentonite solution in the case of a cationic surfactant were introduced into a 20-ml measuring flask. The total volume of the solution was made up to 20 ml with water. A part of the solution was used to measure the initial pH (pH_i) and the Cd^{2+} ion concentration (C_i mol/l). A 10-ml portion of the remaining solution was transferred into the flotation cell, and the gas flow was started. After a definite time of flotation, about a 7-ml portion of the solution was taken out in order to determine the final pH (pH_f) and Cd^{2+} ion concentration (C_f mol/l), the latter being calculated from the absorbance measured at 2288 Å and at pH 2.6 using an atomic absorption spectrometer (Techtron Pty., Ltd., Model-AA-100).

The gas-flow rate was kept constant at 10 ml/min throughout the experiments. The gas-flow time was kept at 7 min unless otherwise stated. The measurements were carried out at room temperature (about 25 °C).

Results and Discussion

In the present work, the effects of the flotation rate on the gas-flow time, the bentonite concentration, the surfactant concentration, and the pH were studied.

The flotation rate (F) of Cd^{2+} ions is conventionally given by:

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

Experiments were mainly run under the conditions of bubble flotation, mainly 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 rate calculated expresses substantially the percentage of Cd^{2+} ions removed from the total solution.

---

* Present address: Department of Chemistry, Musashi Institute of Technology, 1-28-1, Tamatsutsumi, Setagaya, Tokyo 158.

Flotation of Cd^{2+} Ion by Anionic Surfactants. *Relation between Flotation Rate and Gas-flow Time*: In order to study the optimum gas-flow time of various surfactants, flotation experiments were run at the optimum condition of flotation at around pH 11.2. Figure 1 shows the effects of the gas-flow time at the gas-flow rate of 10 ml/min on the flotation rate for the Cd^{2+}–α-SLNa, –DBS, and –SDS systems. It can be seen that the flotation rate attains a steady value after about 7 min, longer than the 2-min gas flow required in the case of Cu^{2+} ion flotation.[1]

Relation between pH and Flotation Rate. Figure 2 shows the effect of the pH on the flotation rate for the Cd^{2+}–SDS system. As may be seen, the flotation rate begins to increase from zero at around pH 8 for the 1.78×10^{-5} mol/l SDS concentration. The pH value is higher than pH 6 in the case of Cu^{2+} ions because of the stronger basic nature of Cd^{2+} ions. When the pH is adjusted using sodium hydroxide, a maximum flotation rate of about 85% was observed at pH 11.3, while the flotation rate was less in the case of the pH adjusted by using ammonia. In the former case, cadmium hydroxide, probably in the form of polynuclear Cd^{2+} ions,[8] is attracted and floated by SDS, whereas in the latter case, the formation of polynuclear Cd^{2+} ions is prevented to a certain extent by the formation of an ammine complex such as $Cd(NH_3)_4^{2+}$, which adsorbs less efficiently than the polynuclear ions. At the large SDS concentration of 8.90×10^{-5} mol/l, a stable foam layer forms and Cd^{2+} ions are floated even below pH 8, showing flotation rates of about 40% for systems with the pH adjusted by both sodium hydroxide and ammonia. This may be explained by the simple adsorption of Cd^{2+} ions on the surface of ascending bubbles, which persist as a stable foam layer and concentrate the Cd^{2+} ions. Thus, the flotation is considered to be an ion-adsorption flotation. Between pH 8 and 10, Cd^{2+} ion flotation is considered to take place either by ion adsorption and precipitation or by ion adsorption and a hindered precipitation mechanism, according to whether sodium hydroxide or ammonia is used to adjust the pH. Beyond pH 10, the curve for the system adjusted by sodium hydroxide shows a maximum and a subsequent decrease due to the competition between OH^- and DS^- ions for Cd^{2+} in the high pH region, while the curve ends before the appearance of a maximum for the system controlled with ammonia due to the weak basicity of ammonia. The flotation was carried out further for the Cd^{2+}–DBS system. A result similar as a whole to Fig. 2 was obtained except that a maximum F value of 95% was obtained at about pH 11.3 for the system containing 1.78×10^{-5} mol/l DBS and the pH adjusted using sodium hydroxide. In other pH regions, however, the flotation rates were less than those of the SDS system. Figure 3 shows the flotation rates for the Cd^{2+}–LNa system, ammonia being used to adjust the pH. In this system, the flotation rate begins to increase at about

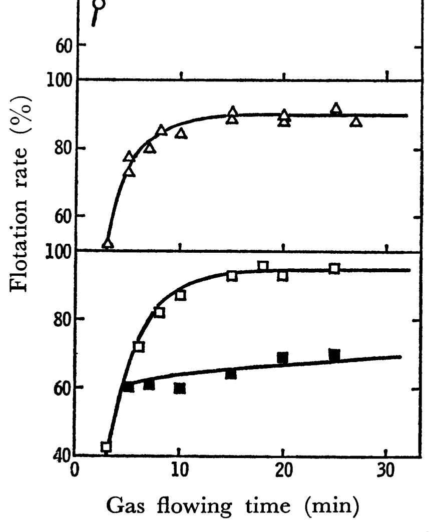

Fig. 1. Flotation rate *vs.* gas-flow time for Cd^{2+}-SDS, -DBS and -α-SLNa systems.
Cd^{2+}: 1.78×10^{-5} mol/l, gas-flow rate: 10 ml/min, α-SLNa: 1.78×10^{-4} mol/l (○: pH_i 11.2), DBS: 1.78×10^{-5} mol/l (△: pH_i 11.2), SDS: 8.90×10^{-5} mol/l (■: pH_i 10.3, □: pH_i 11.2), pH adjusted by NaOH.

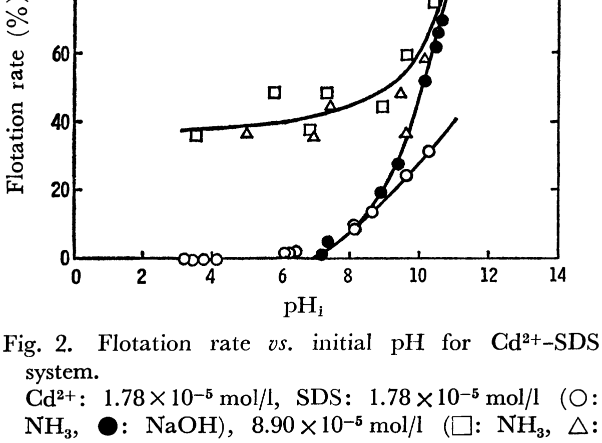

Fig. 2. Flotation rate *vs.* initial pH for Cd^{2+}-SDS system.
Cd^{2+}: 1.78×10^{-5} mol/l, SDS: 1.78×10^{-5} mol/l (○: NH_3, ●: NaOH), 8.90×10^{-5} mol/l (□: NH_3, △: NaOH).

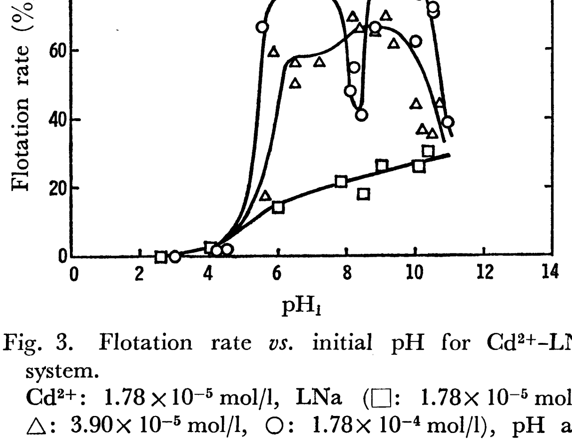

Fig. 3. Flotation rate *vs.* initial pH for Cd^{2+}-LNa system.
Cd^{2+}: 1.78×10^{-5} mol/l, LNa (□: 1.78×10^{-5} mol/l, △: 3.90×10^{-5} mol/l, ○: 1.78×10^{-4} mol/l), pH adjusted by NH_3.

pH 5.5 and sharply decreases at about pH 10.5, at least for the two systems studied. In the acid solution, LNa is hydrolyzed to form uncharged lauric acid, and the flotation may be explained by the Cd^{2+} ions being trapped in or adsorbed by the lauric acid floc. The sharp minimum or the slight step observed in the *F vs.* pH curve near pH 8 also suggests that the precipitation flotation takes place in the region of pH values larger than 8.

Figure 4 shows the *F vs.* pH_i curve for Cd^{2+}–α-SLNa systems of varying surfactant concentrations. The flotation rate increases sharply at around pH 8 and reaches a maximum at around pH 11 for all the systems observed. A maximum *F* value of 97% was observed for the 3.56×10^{-4} mol/l α-SLNa system with its pH adjusted by sodium hydroxide. The flotation rates remain far below those for the system with its pH adjusted by ammonia. The reason for this is the same as has been presented above. The decrease in *F* at higher pH values may be due, in addition to the ionic competition mentioned above, to the formation of $Cd(OH)_4^{2-}$ and $Cd(OH)_5^{3-}$.[9)]

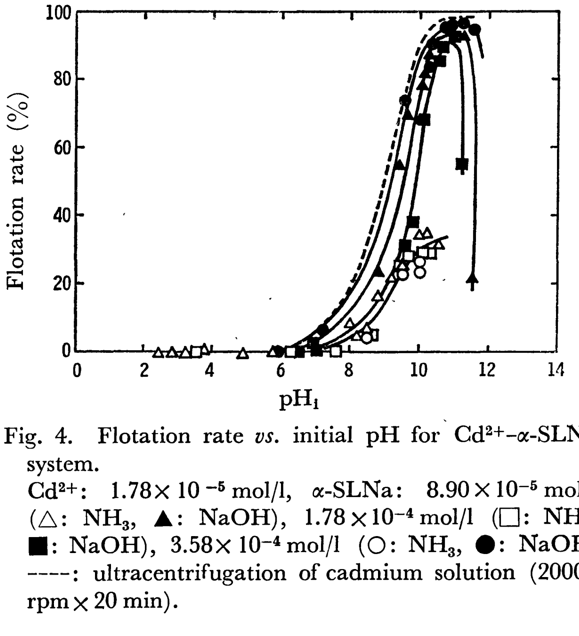

Fig. 4. Flotation rate *vs.* initial pH for Cd^{2+}–α-SLNa system.
Cd^{2+}: 1.78×10^{-5} mol/l, α-SLNa: 8.90×10^{-5} mol/l (△: NH_3, ▲: NaOH), 1.78×10^{-4} mol/l (□: NH_3, ■: NaOH), 3.58×10^{-4} mol/l (○: NH_3, ●: NaOH, ----: ultracentrifugation of cadmium solution (20000 rpm × 20 min).

Further, as may be seen in Fig. 4, the effect of the α-SLNa concentration on *F* was found to be rather small in the region of concentrations studied. It is noticeable that a larger increase in the α-SLNa concentration does not produce foam formation; only the bubble flotation of the precipitate takes place. Thus, the best condition of Cd^{2+} ion flotation is provided by the α-SLNa molecule having both carboxylic and sulfonic groups. The situation is very similar to the case of Cu^{2+} flotation.[1)] These results are further evidence for the view stated previously[1)] that α-SLNa forms a strongly surface-active Cd salt by the carboxylic group, while the sulfonic group protects the salt from precipitation.

It is further shown that the optimum pH of flotation roughly agrees with the pH 11 of the complete removal of Cd^{2+} as hydroxide, which is confirmed by the centrifugal separation, as is also shown in Fig. 4. It was inferred that the existence of a foam layer was not essential for precipitation flotation, although foam formation enhances the ion-adsorption flotation.

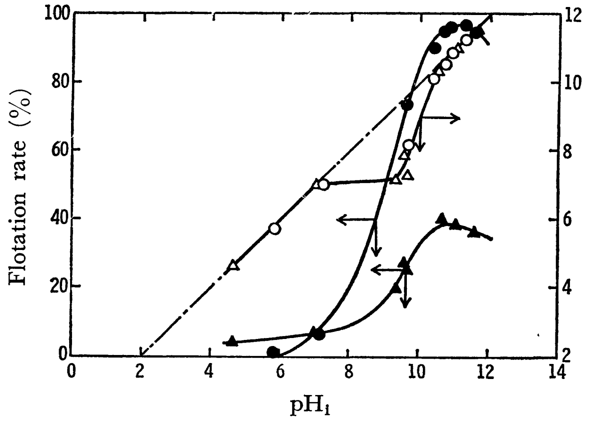

Fig. 5. Initial pH *vs.* final pH and flotation rate for Cd^{2+} and Cd^{2+}–α-SLNa systems.
Cd^{2+}: 1.78×10^{-5} mol/l, α-SLNa: 3.58×10^{-4} mol/l, ○,●: Cd^{2+} system, △,▲: Cd^{2+}–α-SLNa system, pH adjusted by NaOH.

Mechanism of Flotation of Cd^{2+} Ions by Anionic Surfactant. The final pH after flotation is plotted as a function of the initial pH in Fig. 5. The *F vs.* pH curves with and without α-SLNa are also shown in Fig. 5. As may be seen in this figure, a plateau appears in the pH region from about 7 to 9 as a result of the liberation of H^+ ions by the formation of insoluble polynuclear species such as are expressed by:

$$nCd^{2+} + (n-1)H_2O \rightarrow {}^{+}Cd(OCd)_{n-2}OCd^{+} + 2(n-1)H^{+}$$

much as in a previous report.[1)] Again, this is evident that large amounts of Cd^{2+} ions are removed in a polynuclear form by a small amount of a surfactant. A slight flotation was observed by the adsorption or adhesion of polynuclear species on ascending bubbles without any surfactant, but the best flotation was obtained by adding an anionic surfactant. The decrease in the flotation rate below pH 8 seems to be due to the competition between H^+ and Cd^{2+} ions for the anionic surfactant.

Flotation of Cd^{2+} Ion by Cationic Surfactants. Effect of the Time of Gas Flow: Cd^{2+} ions can be floated by a cationic surfactant through a bridge of macromolecular anions like bentonite.

The flotation was carried out for a solution containing 1.78×10^{-5} mol/l Cd^{2+} ions, 1.78×10^{-4} mol/l HTAC, and 0.01% bentonite at pH 11.3. About 98% of the *F* was obtained after a 2-min gas-flow time. It was found that the addition of bentonite markedly reduced the time of gas flow and increases the *F* compared with the case of the Cd^{2+}-anionic surfactant systems of Fig. 1. Thus, the cationic surfanctant-bentonite system is superior to the anionic surfactant system in this respect.

Relation between pH and Flotation Rate. Figure 6 shows the results of the flotation of the Cd^{2+}–bentonite–OBAC system with the gas-flow time of 7 min and with the pH being controlled with sodium hydroxide and ammonia. The flotation rate increases sharply at around pH 8 and shows a maximum of $F=93\%$ at pH 11.3 for the system of pH adjusted by sodium hydroxide,

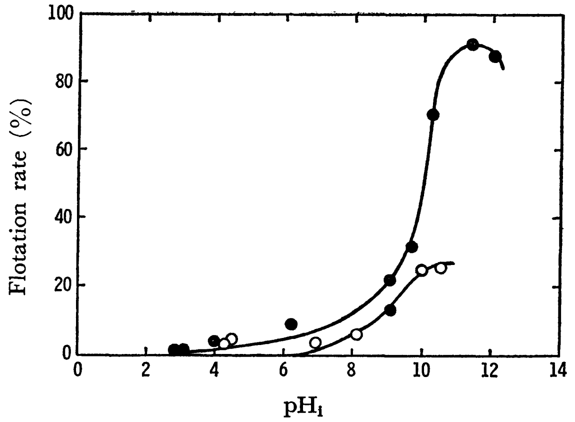

Fig. 6. Flotation rate *vs.* initial pH for Cd^{2+}-bentonite-OBAC system.
Cd^{2+}: 1.78×10^{-5} mol/l, OBAC: 3.56×10^{-5} mol/l, bentonite: 0.001%, ○: pH adjusted by NH_3, ●: pH adjusted by NaOH.

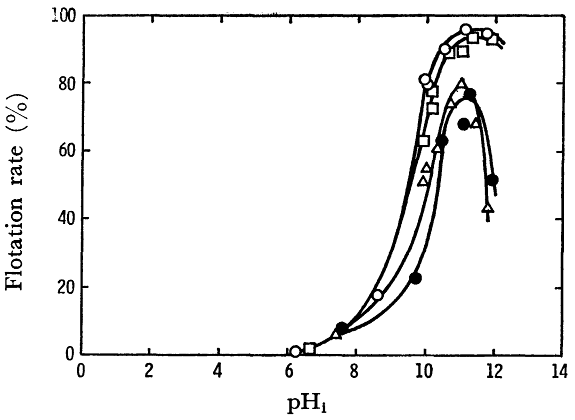

Fig. 7. Flotation rate *vs.* initial pH for Cd^{2+}-bentonite-DTAC system.
Cd^{2+}: 1.78×10^{-5} mol/l, DTAC: 1.78×10^{-4} mol/l, bentonite (●: 0%, △: 0.001%, □: 0.005%, ○: 0.01%) pH adjusted by NaOH.

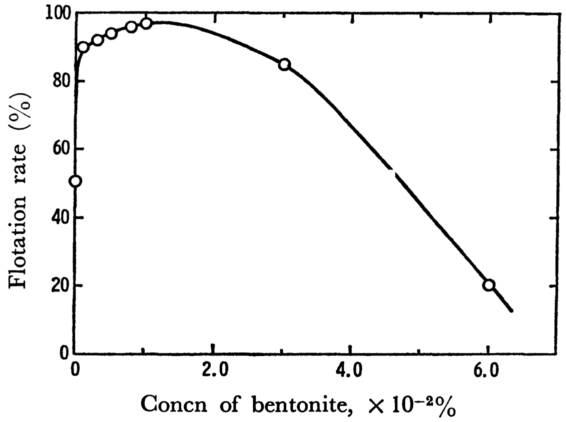

Fig. 8. Flotation rate *vs.* concn of bentonite for Cd^{2+}-bentonite-HTAC system.
Cd^{2+}: 1.78×10^{-5} mol/l, HTAC: 1.78×10^{-4} mol/l, pH adjusted by NaOH.

while a far smaller maximum of $F=30\%$ is obtained for the system of pH controlled using ammonia in the same pH region. The difference may be caused by the reduction of the formation of polynuclear cadmium hydroxide due to ammine complex formation in the latter system mentioned above. In order to see the effect of the pH on the flotation rate, the flotation was carried out for a solution containing 1.78×10^{-5} mol/l Cd^{2+} ions, 1.78×10^{-4} mol/l surfactant, and 0.01% bentonite. No difference in the nature of the cationic surfactant on the flotation rate was observed for the surfactants used in the present study. The flotation rate remains zero up to pH 5, above which it increases gradually up to pH 8.5 and rapidly thereafter. The maximum F of 97% was observed above pH 11.3. As a whole, the F *vs.* pH curve of Cd^{2+} shifts towards a pH higher by two units than that for Cu^{2+} ions. The shift may be due to the stronger basic nature of the former. In the case of Cd^{2+} ion flotation by bentonite and cationic surfactants, Cd^{2+} ions, polynuclear cations, and complex anions such as $Cd(OH)_4{}^{2-}$ combined with the cationic surfactants adsorb on the bentonite particles in this order as the pH of the solution increases, and the bentonite is subsequently coagulated and floated by bubbles. Thus, the flotation may be classified as an adsorbing particle (bubble) flotation. At pH values lower than 8, the flotation rate is largely reduced by the absence of polynuclear Cd^{2+} ions and the suppression of Cd^{2+} ion adsorption of bentonite by H^+ ions.

Effect of Bentonite. To study the effect of bentonite, the F *vs.* bentonite concentration was plotted for DPC, DTAC, and HTAC. Some of the results are shown in Fig. 7 for DTAC. The flotation rates increase and the regions of the flotation range extend up to a certain point with an increase in the amount of bentonite for all the systems studied. For the cationic surfactant with the 1.78×10^{-4} mol/l concentration, the maximum F value of 97% was obtained with the addition of 0.01% bentonite and at pH 11.3, as adjusted by sodium hydroxide. Here, the addition of bentonite also favored the bubble production, without any foam formation. Thus, bentonite acts not only as a bridge between Cd^{2+} ions and bubbles, but also as an inhibitor of foaming due to the surfactant, thus resulting in effective bubble flotation. The flotation was carried out further for a solution containing 1.78×10^{-4} mol/l Cd^{2+}, 2×10^{-4} mol/l HTAC, and varying amounts of bentonite at a gas-flow time of 7 min and a gas-flow rate of 10 ml/min at pH 11. The results are shown in Fig. 8. It was further confirmed that a stable foam layer was produced for the solution containing less than 0.008% bentonite. As may be seen in the figure, the flotation rate increases sharply and then decreases to zero after showing a distinct maximum. The concentration of bentonite favorable for the bubble flotation of Cd^{2+} ions is found to be 0.008—0.015%. The decrease in the flotation rate above 0.015% bentonite may be explained by the surfactant being insufficient to float the bentonite adsorbing Cd^{2+} ions evenly. About 50% of the Cd^{2+} ions are floated even in the absence of bentonite. This may be due to some Cd^{2+} ions being entrapped in or adsorbed on the cationic foam by nonspecific interaction between the cationic surfactant and polynuclear Cd^{2+} or cadmium hydroxide.

Effect of the Concentration of the Surfactant. To study the effect of the concentration of the cationic surfactant, a F *vs.* pH_i curve for varying concentrations of DPC, and DTAC was obtained; it is not shown in the figure, however. The flotation rate decreases from 95 to 73% with a decrease in the DPC concentration from 1.78×10^{-4} to 1.78×10^{-5} mol/l in the case of Cd^{2+} ion flotation by DPC, whereas in the case of Cd^{2+} ion flotation by DTAC the flotation rate did not change with an increase in the concentration of DTAC from 3.56×10^{-5} to 1.78×10^{-4} mol/l above pH 9. Figure 9 shows the F *vs.* surfactant concentration for HTAC at pH 11.3. As may be seen in Fig. 9, the optimum rate of bubble flotation (about 97%) was observed in the region of the HTAC concentration from 8×10^{-5} to 3.56×10^{-4} mol/l. The decrease in the flotation rate for the concentrations of HTAC larger than 3.56×10^{-4} mol/l is caused by both the excessive surfactant repelling Cd^{2+} ions from the surface of bentonite and the bimolecular layer of surfactant adsorption producing hydrophilic bentonite of a poor flotability. The decrease in the flotation rate in the low-surfactant-concentration region may be explained as resulting from the surfactant being insufficient to float the bentonite.

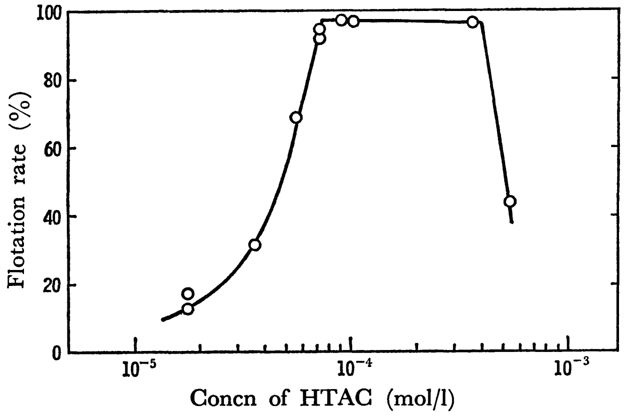

Fig. 9. Flotation rate *vs.* concn of HTAC for Cd^{2+}–bentonite–HTAC system.
Cd^{2+}: 1.78×10^{-5} mol/l, bentonite: 0.01%, pH_i: 11.2, pH adjusted by NaOH.

In conclusion, Cd^{2+} ions could be efficiently floated by using an anionic surfactant or a cationic surfactant with bentonite, and the ion-flotation method can be effectively used under such conditions for the removal of Cd^{2+} ions from sewage and waste water.

The author wishes to thank Professor Tsunetaka Sasaki of the Tokai University for his valuable discussion and suggestions.

References

1) K. Kobayashi, This Bulletin, **48**, 1180 (1975).
2) R. Lemlich, "Adsorptive Bubble Separation Techniques," Academic Press, New York and London (1972).
3) F. Sebba, "Ion Flotation," Elsevier Publisher London and New York (1962).
4) R. Lemlich, "Adsorptive Bubble Separation Techniques," Academic Press, New York and London (1972), pp. 219—245.
5) J. Shimoiizaka, S. Hasebe, I. Matsuoka, T. Takahashi, and K. Yamamoto, *J. Min. Assoc. Jap.*, **86**, 549 (1970).
6) T. Goto and G. Izumi, *Nippon Kagaku Kaishi*, **7**, 1315 (1974).
7) B. B. Ferguson, C. Hinkle, and D. J. Wilson, *Separ. Sci.*, **9**, 125 (1974).
8) F. Sebba, "Ion Flotation," Elsevier Publisher, London and New York (1962), p. 57.
9) G. Charlot, "L'analyse Qualitative et Les Réactions en Solution," Masson et C^{ie}. Editeurs (1957).