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

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The effects of several anionic surfactants—sodium α-sulfolaurate, sodium laurate, sodium dodecylsulfate, and cationic surfactants, dodecylpyridinium chloride, and dodecyltrimethylammonium chloride—on the bubble flotation of Cu^{2+} ions were studied. Sodium α-sulfolaurate was found to be most effective for the flotation of Cu^{2+} ions. The flotation rate (percent removed) increased sharply from zero at about pH 6, and a rate larger than 95% was attained in the pH region of about 7 to 11. Cationic surfactants alone could float Cu^{2+} ions only slightly. They floated most of the Cu^{2+} ions upon the addition of bentonite, however. A flotation rate of about 90% was attained in the pH region larger than about 6. This was explained by the Cu^{2+} ions being removed as polynuclear species, which combined directly with an anionic surfactant or a cationic surfactant with the aid of bentonite.

The foam separations of soluble and suspended matters in water have drawn increasing attention in connection with industrial waste water,[1,2] sewage treatment,[1,2] the removal of trace amounts of radioactive substance from solutions[3] and the concentration of rare elements from sea water.[4,5] The techniques of ion flotation involve the removal of surface inactive ions from aqueous solutions with the aid of bubbles and can be divided into several processes differing in detail, such as adsorption flotation, precipitation flotation, and adsorbing-particle flotation.[6] The adsorption flotation consists of the flotation of ions in a solution by adsorption on ascending bubbles. In the precipitation flotation, ions in the solution are precipitated by the addition of proper substances or by controling the pH, and the precipitates formed are floated by adding a surfactant. The adsorbing-particle flotation consists of the adsorption of ions from a solution on adsorbent particles like bentonite or a synthetic ion-exchanger; the ions are subsequently floated by the addition of a suitable surfactant. The adsorption flotation requires a stoichiometric or greater concentration of surfactants, while in the case of precipitation flotation relatively small amounts of surfactants are sufficient. A preliminary experiment showed that the adsorbing-particle flotation was the most efficient among these methods of flotation.[7]

The ion-adsorption flotation was first introduced by Sebba,[8] and the ion-precipitation flotation, by Baarson and Ray.[9] Rubin *et al.*[10] compared the effects of several variables on these processes. Recently a number of studies of ion adsorption and precipitation flotations from theoretical points of view have been reported,[11,12] but much remains unsolved.

The present work has been undertaken in order to study the flotation of Cu^{2+} ions by a number of surfactants from the surface-chemical point of view, under varying conditions of pH, gas-flow rate, time, and concentrations of the surfactants and Cu^{2+} ions.

Experimental

Materials. The cupric sulfate used was a reagent-grade $CuSO_4 \cdot 5H_2O$; it was recrystallized from distilled water, and stock solutions of 2×10^{-3} and 1×10^{-3} mol/l concentrations were prepared.

The surfactants used included sodium *n*-dodecylsulfate (SDS), sodium *n*-dodecylbenzenesulfate (DBS), sodium laurate (LNa), and sodium α-sulfolaurate (α-SLNa) as anionic surfactants, and *n*-dodecylpyridinium chloride (DPC) and *n*-dodecyltrimethylammonium chloride (DTAC) as cationic surfactants.

The SDS was synthesized from dodecanol and chlorosulfonic acid, and the product was purified by extraction with ethyl ether and recrystallization from ethanol.[13] Pure-grade DBS was supplied by the Kao Soap Co., Ltd., and was dried over phosphorus pentoxide. A reagent-grade LNa, a product of the Tokyo Kasei Industrial Co., Ltd., was recrystallized from ethanol with water. The α-SLNa, a product of the Kao Soap Co., Ltd., was recrystallized from ethanol with a little water. The DPC and DTAC, products of the Tokyo Kasei Industrial Co., Ltd., were recrystallized from acetone and ethanol respectively; the latter was washed with ether and dried. These surfactants were kept in a desiccator. The aqueous solutions were prepared before use.

The bentonite powders used as ion-exchange adsorbents were obtained from the Wako Pure Chemical Co., Ltd.; the fraction passing through a 350-mesh sieve was collected, and a suspension of 0.01 g/l concentration was made and used after shaking before each experiment. The pH of the solution was controlled by using sulfuric acid and sodium hydroxide of an extra pure grade. The water used was triply distilled; it was found to be free from Cu^{2+} ions by the use of an atomic absorption spectrometer.

Apparatus and Procedure. The apparatus used is shown in Fig. 1. Nitrogen gas from a nitrogen cylinder, A; successively passing through a gas filter, B; a manostat, C; an empty chamber, D, and a humidifier, E, saturated with water, was introduced into a flotation cell, G, at a constant rate of flow controlled with a calibrated capillary flow meter, F. The flow rate of the nitrogen gas was measured by

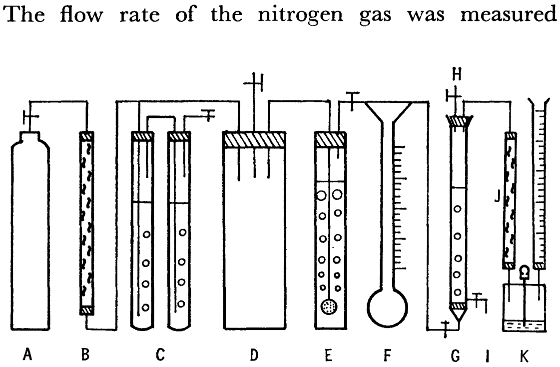

Fig. 1. Apparatus for ion flotation.
A: N_2 gas cylinder, B: glass filter, C: manostat, D: empty chamber, E: humidifier, F: capillary flow meter, G: flotation cell (No. 4), H: inlet, I: outlet J: glass filter, K: soap film flow meter.

means of a soap-film flow meter, K; after the gas has been filtered through a glass wool filter, J. The flotation cell used was a glass column, 32.0 cm long and 1.0 cm in inner diameter, equipped with a sintered glass plate with a porosity of No. 4.

The sample liquid was introduced into the cell from an inlet, H, and the residual solution after flotation was withdrawn from an outlet, I, for the measurements of the Cu^{2+}-ion concentration and the pH. The concentration of the Cu^{2+} ions was measured by using an atomic absorption spectrometer (Techtron Pty., Ltd., Model–AA–100). The absorbance was measured at 3248 Å. A glass electrode pH meter (Toadenpa Co., Ltd., HM–5A) was used to measure the pH. For the measurement of the flotation, 2 ml of a stock solution of 1×10^{-3} or 2×10^{-3} mol/l Cu^{2+} ions, a small amount of a sodium hydroxide or sulfuric acid solution to adjust the pH to a desired value, 2 ml of a bentonite suspension in the case of a cationic surfactant, and 2 ml of a surfactant solution were introduced successively into a 20-ml measuring flask; the total volume was then made 20 ml with water. About 10 ml of the sample solution thus prepared was used to measure the initial pH (pH_i). Ten ml of the remaining solution was transferred to the flotation cell, the gas flow was started, and flotation was carried out as has been described above. The gas-flow rate was kept at 10 ml/min for all the experiments except for the study of the effect of the gas-flow rate. The gas-flow time was kept at 2 or 7 min unless otherwise stated. After the flotation, about 7 ml of the solution was taken out of the flotation cell for the measurements of the final pH (pH_f) and the Cu^{2+}-ion concentration (C_f). The measurements of the flotation were carried out at a room temperature of about 25 °C.

Results and Discussion

The flotation rate, $F(\%)$, of Cu^{2+} ions is conventionally expressed by:

$$F = (1 - C_f/C_i)\times100$$

where C_i denotes the initial concentration of Cu^{2+} ions.

All the experiments were run under the conditions of bubble flotation—namely, flotation using only ascending bubbles, without the aid of foam formation. Since the solution was made uniform in concentration by bubbling, and since most of the solution after flotation was used for the determination of the Cu^{2+}-ion concentration, the F measured substantially expresses the total percentage of Cu^{2+} ions removed from the solution.

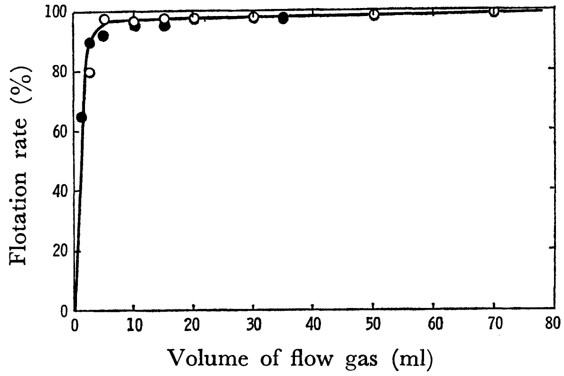

Fig. 2. Flotation rate *vs.* volume of flow gas for Cu^{2+}–α-SLNa system.
Cu^{2+}: 2×10^{-4} mol/l, α-SLNa: 4×10^{-4} mol/l, pH_i: 9.3, gas-flow rate: ○; 10 ml/min, ●; 5 ml/min.

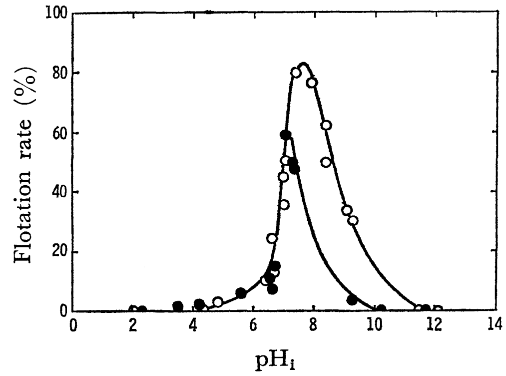

Fig. 3. Flotation rate *vs.* initial pH for Cu^{2+}-SDS system.
Cu^{2+}: 2×10^{-4} mol/l, SDS: 1×10^{-5} mol/l, gas-flow time: ●; 2 min, ○; 7 min.

(1) *Flotation of Cu^{2+} Ions by Anionic Surfactants. Relation between the Volume of the Flow Gas and the Flotation Rate*: Figure 2 shows the flotation rate as a function of the total volume of the gas flow at various rates for the Cu^{2+}–α-SLNa system. The figure shows that the flotation rate is simply a function of the volume of the gas flow and is independent of the flow rate. This is in accord with Rubin's view[14] that the flotation rate depends only on the volume of the gas flow. In the present case, F of nearly 100% is obtained, at least after 10 ml of nitrogen gas has flowed. Accordingly, all subsequent experiments were run at a gas-flow rate of 10 ml/min and a gas-flow time of 2 or 7 min.

Relation between the pH and the Flotation Rate. Figure 3 shows the effect of the pH on the flotation rate for the 2×10^{-4} mol/l Cu^{2+} and 1×10^{-5} mol/l SDS systems. As may be seen in this figure, the flotation rate increases sharply at about pH 6 and reaches its maximum at a pH value from 7 to 8 for the gas-flow times of both 2 and 7 min. An F of about 80% is obtained at the gas-flow time of 7 min. Beyond a 1×10^{-5} mol/l SDS concentration, the condition of bubble flotation changes to that of froth flotation, which was not studied since excessive foaming results in a large hold-up of the solution, thus preventing effective bubble flotation.

Figures 4 and 5 show the F *vs.* the gas-flow time and the F *vs.* surfactant concentration curves respectively for the Cu^{2+}–α-SLNa system. It may be seen in Fig. 3 that, at a 1×10^{-5}mol/l SDS concentration, the flotation rate increases with the gas-flow time. A similar effect may be expected for the Cu^{2+}–α-SLNa system, considering the same rate of flotation for the 1×10^{-5} mol/l α-SLNa concentration and the gas-flow time of 7 min. At a 4×10^{-4} mol/l α-SLNa concentration, the rate increases and shows a flat maximum of F of 98% extending from pH 7 to 11, independent of the gas-flow time, while for the SDS system the increase in the SDS concentration from 1×10^{-5} to 1×10^{-4} mol/l results in both an excessive foaming and hold-up of the solution, as has been mentioned above.

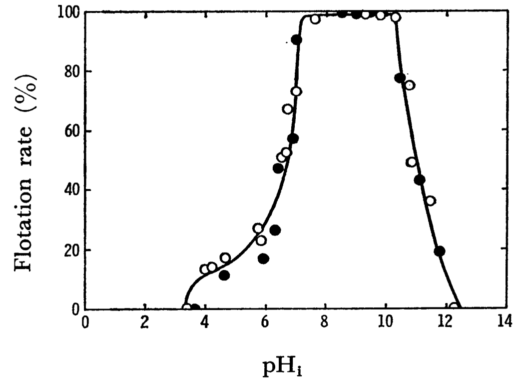

Fig. 4. Flotation rate vs. initial pH for Cu^{2+}-α-SLNa system.
Cu^{2+}: 2×10^{-4} mol/l, α-SLNa: 4×10^{-4} mol/l, gas-flow time: ●; 2 min, ○; 7 min.

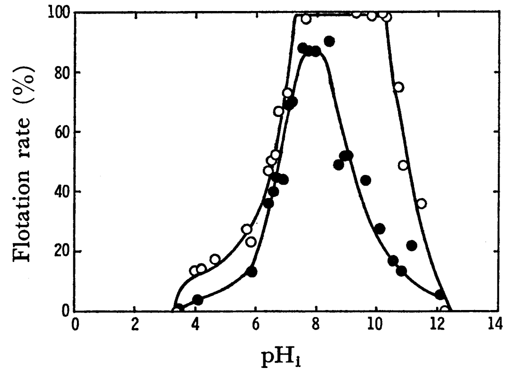

Fig. 5. Flotation rate vs. initial pH for Cu^{2+}-α-SLNa system.
Cu^{2+}: 2×10^{-4} mol/l, α-SLNa: ○; 4×10^{-4} mol/l, ●; 1×10^{-5} mol/l, gas-flow time: 7 min.

This may indicate that α-SLNa is superior to SDS as the additive for Cu^{2+} flotation, and confirms the view that the introduction of a carboxylic group into alkylsulfate increases the flotation efficiency.[15)]

Figure 6 shows the pH dependence of the flotation rate for the Cu^{2+}–LNa system. The behavior is similar to that of the Cu^{2+}–α-SLNa system, showing a broad maximum, but a somewhat lower F value than that of the Cu^{2+}–α-SLNa system. Figure 7 shows the F vs. pH curve for the Cu^{2+}–DBS system. The rate of flotation, like that of Cu^{2+}–LNa system, shows a sharp increase at pH 6. On a further increase in the pH, a plateau or a minimum appears after a slight maximum, and then marked maxima at pH 10 appear, showing an F of 96% for DBS at the concentration of 2×10^{-5} mol/l. The system of 1×10^{-4} mol/l DBS exhibits stable foam formation, and so it was not studied. The Cu^{2+}–DBS system is seen to be intermediate in behavior between the Cu^{2+}–SDS and Cu^{2+}–α-SLNa systems.

Mechanism of Flotation of Cu^{2+} Ions by Means of an Anionic Surfactant. When we compare Figs. 3, 4 and 6, the cooperative effect of sulfate and carboxylic groups is evident. It may be explained by the fact that the presence of carboxylic groups is effective for the bubble flotation by combining with Cu^{2+} ions, while the coexistence of sulfonic groups enhances the flotation rate by increasing the solubility of the collector, as has previously been reported.[11)]

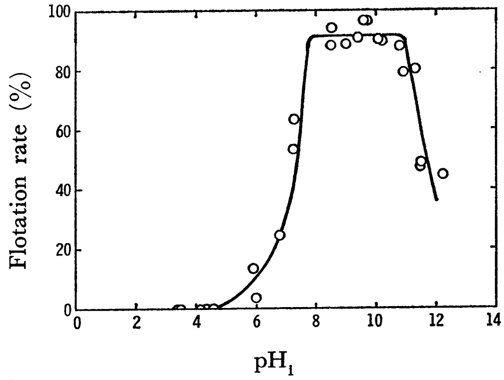

Fig. 6. Flotation rate vs. initial pH for Cu^{2+}-LNa system.
Cu^{2+}: 1×10^{-4} mol/l, LNa: 2×10^{-4} mol/l, gas-flow time: 7 min.

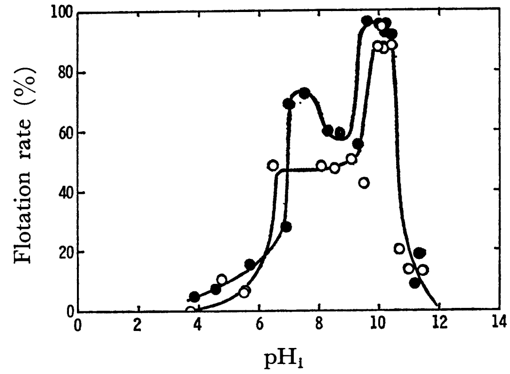

Fig. 7. Flotation rate vs. initial pH for Cu^{2+}-DBS system.
Cu^{2+}: 1×10^{-4} mol/l, DBS: ○; 1×10^{-5} mol/l, ●; 2×10^{-5} mol/l, gas-flow time: 7 min.

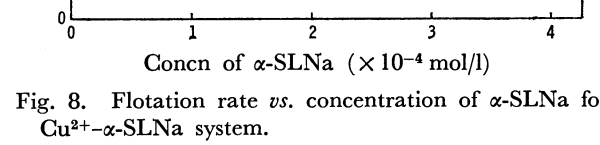

Fig. 8. Flotation rate vs. concentration of α-SLNa for Cu^{2+}-α-SLNa system.
Cu^{2+}: 2×10^{-4} mol/l, pH$_i$: 9.30—9.50, gas-flow time: 7 min.

As has been mentioned above, Figs. 3—7 show sharp rises in the F vs. pH curves at pH 6, which correspond to the beginning of copper-hydroxide precipitation. This might indicate that the sublate consists mainly of a polynuclear hydroxide-surfactant complex, the process being called the precipitation flotation of the first type.[16)] Figure 8 shows the effect of the concentration of α-SLNa on the rate of the

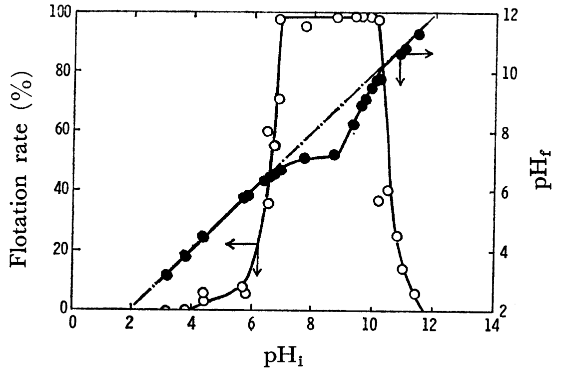

Fig. 9. Initial pH *vs.* final pH and flotation rate for Cu^{2+}-α-SLNa system.
Cu^{2+}: 1×10^{-4} mol/l, α-SLNa: 2×10^{-4} mol/l, gas-flow time: 7 min.

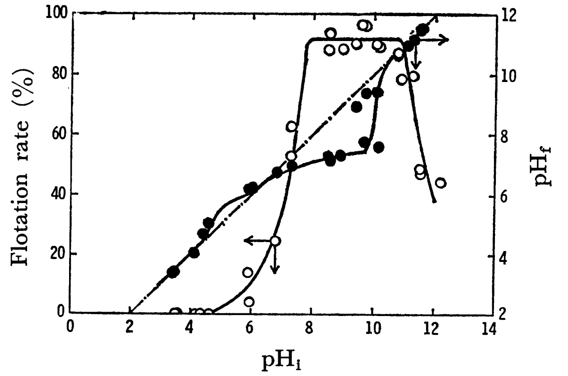

Fig. 10. Initial pH *vs.* final pH and flotation rate for Cu^{2+}-LNa system.
Cu^{2+}: 1×10^{-4} mol/l, LNa: 2×10^{-4} mol/l, gas-flow time: 7 min.

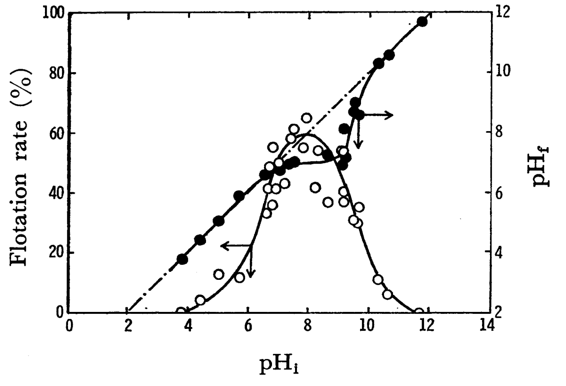

Fig. 11. Initial pH *vs.* final pH and flotation rate for Cu^{2+}-SDS system.
Cu^{2+}: 1×10^{-4} mol/l, SDS: 1×10^{-5} mol/l, gas-flow time: 7 min.

flotation of the 2×10^{-4} mol/l Cu^{2+} solution. It may be seen in this figure that F of nearly 100% is obtained at the surfactant concentration of about 1×10^{-4} mol/l, which is equivalent to one-fourth of the Cu^{2+} ion concentration of this solution. It may be suggested that one surfactant molecule combines with at least four Cu^{2+} ions for a 100% flotation. It may similarly be estimated that the SDS/Cu^{2+} ratio is lower than 1/40 for the Cu^{2+}–SDS system. These small collector/colligend ratios may be considered to be specific for the precipitation flotation of the first type as compared with the case of ion-adsorption flotation, where the surfactants combine with Cu^{2+} ions at a stoichiometric or greater ratio.[17] This also confirms that the precipitation flotation is the dominant factor in the present case.

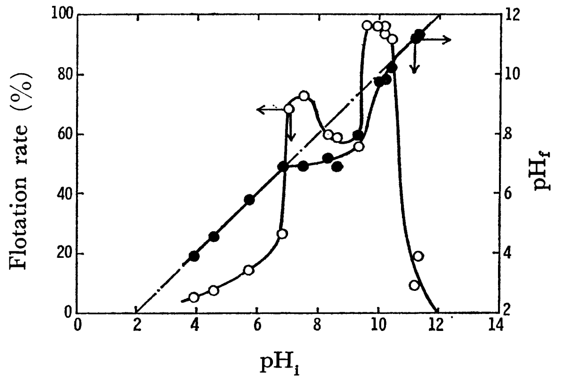

Fig. 12. Initial pH *vs.* final pH and flotation rate for Cu^{2+}-DBS system.
Cu^{2+}: 1×10^{-4} mol/l, DBS: 2×10^{-5} mol/l, gas-flow time: 7 min.

In Figs. 9, 10, 11 and 12, the values of pH$_f$ and F are plotted against the pH$_i$ for the flotation of Cu^{2+} by α-SLNa, LNa, SDS, and DBS respectively. As may be seen in these figures, the plateau appears in the pH$_f$ *vs.* pH$_i$ curve in the vicinity of pH 8. This may be explained by the liberation of hydrogen ions due to the formation of polynuclear species,[11,18] according, for instance, to

$$n\mathrm{Cu}^{2+} + (n-1)\mathrm{H_2O} \rightarrow {}^{+}\mathrm{Cu(OCu)}_{n-2}\mathrm{OCu}^{+} + 2(n-1)\mathrm{H}^{+}$$

This may also explain the fact that large amounts of Cu^{2+} ions are removed by a small amount of a surfactant. The decrease in the flotation rate on the alkaline side is due to the competition between OH$^-$ and surfactant anions for polynuclear Cu^{2+} ions; therefore, the pH region of the decreasing branch and the shape of the maximum of the F *vs.* pH curve depend on the nature of the acid groups.

It is also confirmed that the plateau region of the pH$_f$ *vs.* pH$_i$ curve and the maximum region of the F *vs.* pH$_i$ curve coincide with each other as a whole; this again indicates the formation of a polynuclear Cu^{2+}-surfactant complex, as has been mentioned above. The decrease in the flotation rate of Cu^{2+} ions below pH 6 can be explained by the competition between H$^+$ and Cu^{2+} ions for the anionic surfactant.

Now, in the case of α-SLNa system, the question arises as to whether the polynuclear Cu^{2+} ion attaches to the carboxylic or the sulfonic group of the surfactant molecule. It may be expected, from the similarity of the F *vs.* pH$_i$ curve of α-SLNa to that of the LNa curve (Fig. 6), and from a consideration of the solubility product, that the combination between the Cu^{2+} ion and the carboxylic-acid group is preferred, although Davis and Sebba have reported that the Sr^{2+} ions reacted preferentially with sulfonic groups.[15] The exact determination requires further study.

(2) *Flotation of Cu^{2+} Ions by Means of a Cationic Surfactant.* *Results Obtained*: Figure 13 indicates

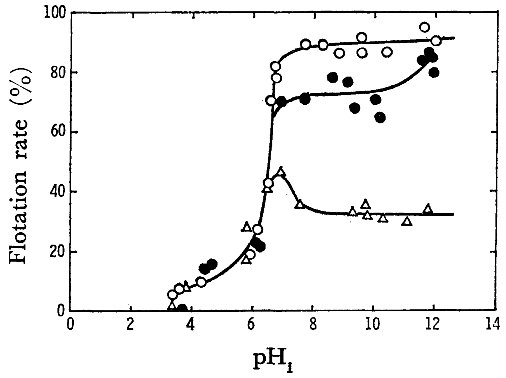

Fig. 13. Flotation rate *vs.* initial pH for Cu^{2+}-DTAC system.
Cu^{2+}: 1×10^{-4} mol/l, DTAC: 2×10^{-4} mol/l, bentonite: △; 0.001%, ●; 0.005%, ○; 0.01%, gas-flow time: 7 min.

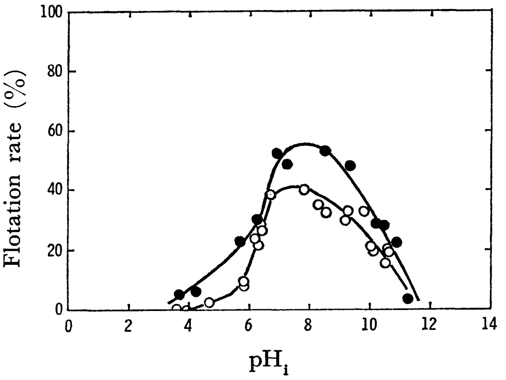

Fig. 14. Flotation rate *vs.* initial pH for Cu^{2+}-DPC system.
Cu^{2+}: 1×10^{-4} mol/l, DPC: 1×10^{-5} mol/l, bentonite: ○; 0%, ●; 0.01%, gas-flow time: 7 min.

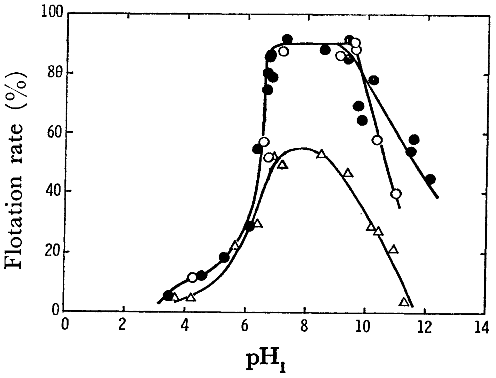

Fig. 15. Flotation rate *vs.* initial pH for Cu^{2+}-DPC system.
Cu^{2+}: 1×10^{-4} mol/l, bentonite: 0.01%, DPC: △; 1×10^{-5} mol/l, ○; 1×10^{-4} mol/l, ●; 2×10^{-4} mol/l, gas-flow time: 7 min.

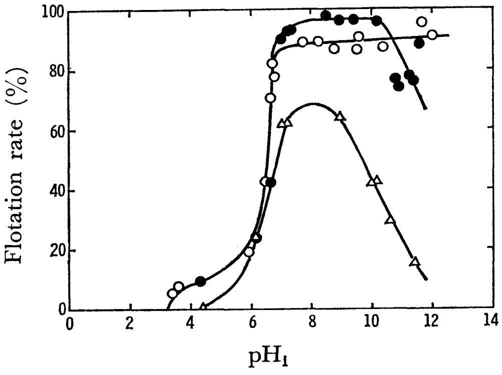

Fig. 16. Flotation rate *vs.* initial pH for Cu^{2+}-DTAC system.
Cu^{2+}: 1×10^{-4} mol/l, bentonite: 0.01%, DTAC: △; 1×10^{-5} mol/l, ●; 1×10^{-4} mol/l, ○; 2×10^{-4} mol/l, gas-flow time: 7 min.

the plots of the flotation rate *vs.* the amount of bentonite for DTAC at various pH values. Figure 14 shows the flotation rate *vs.* the pH curve for DPC with and without the addition of bentonite. Figures 15 and 16 show the relationship between the flotation rate and the surfactant concentration for DPC and DTAC respectively at various pH values.

Relation between the pH and the Flotation Rate. As may be seen in Figs. 13 to 16, the flotation rate remains almost zero for the systems of both DPC and DTAC up to pH 6, above which point it increases much as in the cases of anionic surfactants; a maximum appears in the pH region from 7 to 10 or more. The flotation rate generally decreases in a sufficiently high pH region. In the case of Cu^{2+}-ion flotation by bentonite and a cationic surfactant, bentonite enhances the flotation by the adsorption of Cu^{2+} ions, followed by coagulation and flotation, since a system lacking bentonite markedly decreases the flotation rate, as will be discussed later. Thus, this flotation is classified as an ion-adsorbing particle flotation.[6] Bentonite, being considered as an macromolecular anion, acts as a bridge between the cationic Cu^{2+} ions and the cationic surfactant. The region of large F extends to a higher pH region for the Cu^{2+}–bentonite–cationic surfactant system (Fig. 16) than for the Cu^{2+}–anionic surfactant system (Fig. 5) because, in the former system, the multiple points of attachment are supplied by bentonite for the polynuclear Cu^{2+} ions and the cationic surfactant, while in the latter system the anionic surfactant offers for less site for the polynuclear Cu^{2+} ions. This results is not only an extension of the pH region to a higher value, but also a larger flotation rate of the Cu^{2+}–bentonite–cationic surfactant complex than that of the Cu^{2+}–anionic surfactant. At a sufficiently high pH, OH^- ions compete with bentonite for both cationic surfactant and Cu^{2+} ions in the case of a dilute surfactant or a surfactant of a relatively weak base, and a general tendency for F to decrease is expected, as can be seen for DPC in Figs. 14 and 15 and for DTAC in Fig. 16. A marked decrease in F above pH 10 in the case of the Cu^{2+}–bentonite–DPC system was found to be a result of the weaker basic nature of DPC than of DTAC, as confirmed by the potentiometric titration. At pH values lower than 6, the flotation rate is practically zero for Cu^{2+}–bentonite–cationic surfactant systems; this is a result of the strong adsorption of H^+ on bentonite, which prevents the adsorption of the cationic surfactant and Cu^{2+} ions.

Effect of Bentonite. As may be seen in Fig. 13, an increase in the bentonite concentration from 0.001

to 0.01% increases the flotation rate for the DTAC system. This is a result of the decrease in liquid hold-up by the suppression of foaming and the maintenance of the condition of bubble flotation. The system lacking bentonite strongly foams, so it could not be studied by the bubble-flotation system. Therefore, bentonite acts not only as a bridge between Cu^{2+} ions and bubbles, but also as an inhibitor of foaming caused by the surfactant, thus making effective bubble flotation possible. The complete removal of bentonite, however, exhibited some residual flotation rate, as is shown in Fig. 14 for the Cu^{2+}–DPC system. This may be due to some Cu^{2+} ions being adsorbed on the cationic foam, even in the absence of bentonite, perhaps by a nonspecific interaction between the polynuclear Cu^{2+} ions and the cationic surfactant.

Effect of the Concentration of the Surfactant. As may be seen in Figs. 15 and 16, the flotation rate increases with an increase in the concentration of the surfactant, and reaches a maximum, showing F values of 90% for the 1×10^{-4} mol/l DPC system and 98% for the 1×10^{-4} mol/l DTAC system. Under these conditions, the solutions after flotation look quite transparent and seem free from suspended matter. Therefore, the concentration of the 1×10^{-4} mol/l cationic surfactant is just sufficient for the flotation of both 1×10^{-4} mol/l Cu^{2+} and 001% of bentonite under the present conditions of measurement. The incomplete flotation shown in Figs. 15 and 16 can also be interpreted as resulting from the surfactant being insufficient to float the bentonite. It shoud be noted, however, that the decrease in the surfactant to 1/10 of the optimum concentration only reduces the flotation rate to more than half the optimum value.

It has been reported that the base-exchange capacity of clay mineral ranges from 70 to 150 m eq./100 g.[19] Using the values of 70 m eq./100 g clay, 1×10^{-4} mol/l Cu^{2+}, 0.01% bentonite, and 2×10^{-4} mol/l surfactant, 1000 g of a solution contains 0.07 meq. of exchange sites due to bentonite, 0.2 m eq. of Cu^{2+}, and 0.2 meq. of the surfactant. Therefore, a nearly complete flotation of Cu^{2+} requires a Cu^{2+} polynuclear structure of far less effective equivalence and only a partial adsorption of the surfactant on a limited area on the bentonite surface. The details of such a structure will be reported elsewhere.

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