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The Flotation of Cation by Cationic and Anionic Surfactants

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The ion flotation of a cation by a cationic surfactant with the aid of an anionic chelating agent was studied for the system of Fe^{3+} - ethylenediaminetetraacetic acid (EDTA) - octadecyldimethylammonium chloride (ODAC). The systems of Fe^{3+}-EDTA and Fe^{3+}-ODAC were also studied for purposes of comparison. The effects of the concentration of the above three components, the pH and the gas-flow time on the flotation efficiency were measured. The diagram of the flotation efficiency vs. the pH showed a W-shaped curve for the Fe^{3+}-EDTA-ODAC system, which was explained by the formation of Fe^{3+}-EDTA, Fe^{3+}-ODAC and Fe^{3+}-EDTA-ODAC complexes, each of which has a different optimum pH region of its formation. The flotation of a cation by an anionic surfactant was also studied using ferric, ferrous, silver and Malachite Green ions as cations and sodium dodecylsulfate (SDS) as an anionic surfactant. The flotation efficiency increased with the time of the gas flowing, except for the system of Fe^{3+}-SDS. Such an increase was explained by the relatively insoluble nature of the corresponding SDS salts.

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Recently, the technique of the ion flotation or the foam fractionation** has been receiving increasing attention, from both the practical and the theoretical points of view,[1] due chiefly to their remarkable efficiency in ion separation and concentration in dilute aqueous solutions. In the usual practice of ion flotation, ions in a solution are collected by the foam produced by an ionic surfactant of the charge opposite to that of the ion to be floated.[2] Thus, metallic cations are floated, for instance, by sodium dodecylsulfate (SDS). However, the possibilities have not yet been fully studied of floating ions by an ionic surfactant of the same sign, with or without the addition of a chelating agent or "collector" electrolyte which has the electric charge opposite in sign to both of them and so acts as a bridging ion between the surfactant and the metallic ions.

The present paper will describe the results of an ion flotation study from such a point of view, a study chiefly of the Fe^{3+} - ethylendiaminetetraacetic acid (EDTA) - octadecyldimethylammonium chloride (ODAC) system. The ordinary ion flotation of a cation by an anionic surfactant will also be studied for the sake of comparison.

Experimental

Materials.—Cations used for separation: ferric and ferrous ions as sulfates, silver ion as nitrate, and Malachite Green ion as the corresponding dye salt.

Chelating agent used as a collector: ethylenediaminetetraacetic acid (EDTA).

Foaming agents: octadecyldimethylammonium chloride (ODAC) and sodium dodecylsulfate (SDS).

The ferric, ferrous and silver salts were purified by recrystallization, while the rest of the reagents of chemically-pure grade were used without purification.

Apparatus and Procedure.—The apparatus used in the foam separation experiment is shown in Fig. 1A. By means of a circulation pump, A, air moistened by passing it through the chamber, B, filled with wet cotton wool was introduced, at room temperature (20—25°C) into 50 cc. of the sample solution contained in the cell, D (32 cm. long and 2.5 cm. in diameter), from the the tip, C, about 0.3 mm. in diameter. The rate of gas flow was kept at 1.04 cc./sec. The gas-flow time was kept at 10 min. unless otherwise stated. The foam thus produced was made to overflow and was collected in the chamber, E, where it was cooled by a freezing mixture, F, to about −8°C and thus collapsed. The volume of the collapsed foam was usually about 0.7 cc. for 10 mins' foaming. The concentration of the cation in this solution was determined as follows.

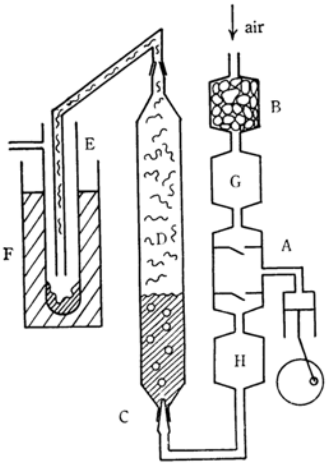

Fig. 1A. Ion flotation apparatus for stable foam.
A, circulation pump; B, chamber filled with wet cotten wool; C, glass tip; D, ion flotation column; E, foam liquid receiver; F, freezing mixture; G and H, empty chambers.

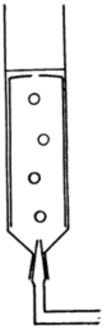

Fig. 1B. Ion flotation apparatus for unstable foam.

Ferric and ferrous ions: Concentrated sulfuric acid and nitric acid were added to the liquid, and the mixture was heated to destroy the organic matter. The ferric ion was then reduced to the ferrous ion by hydroquinone, and after o-phenanthroline had been added, the ferrous ion concentration was determined at a pH value of about 4.5 by the light absorption at 508 Å, using a Beckmann spectrophotometer.

Malachite Green ion: The light absorption was measured at 615 Å, using a Beckmann spectrophotometer.

Silver ion: The concentration was determined by potentiometry using a cell consisting of a calomel electrode and a silver electrode. The foaming agent present did not interfere with the measurement.

The Efficiency of Ion Flotation.—The efficiency of ion flotation may be differently expressed according to whether we refer to the separation, the purification, the extraction or the concentration of ions in question. In the present case, we are chiefly interested in the concentration of cations. Therefore, the efficiency may be conventionally expressed by the ratio:

$$R = X/Y$$

where X is the concentration of ions in the solution obtained by collapsing the foam, and Y, the concentration of the same ions in the initial sample solution.

Results and Discussion

Numerous factors, such as the nature and concentration of the collector, the foaming agent, the ions to be floated and other additives, the time and rate of gas-flow, the temperature of the solution and the construction of the flotation cell, influence the efficiency of ion flotation. Of these,

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** Some authors distinguish these two processes according to whether the separation or fractionation of the solutes occurs exclusively on bubbles in a solution or chiefly on films of foam upon a solution. In the present paper, however, the term " ion flotation" will be used for the sake of the brevity and convenience, though the process adopted is actually a case of foam fractionation.

1) F. Sebba, " Ion Flotation," Elsevier Publisher, Amsterdam, London, New York (1962); H. Kishimoto, *Kolloid-Z.*, **192**, 66 (1963); C. A. Brunner and D. G. Stephan, *Ind. Eng. Chem.*, **57** No. 5, May, 40 (1965).

2) F. Sebba, *Nature*, **184**, 1062 (1959).

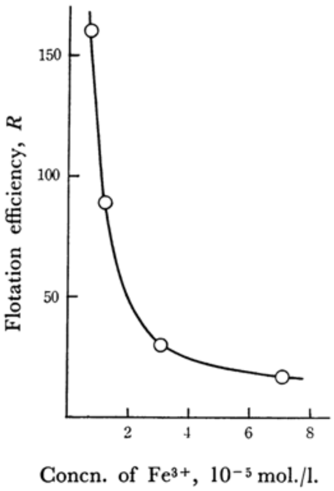

Fig. 2. Flotation efficiency vs. concn. of Fe^{3+} for Fe^{3+}-EDTA-ODAC system.
ODAC 3.02×10^{-4} mol./l.
EDTA 1.102×10^{-4} mol./l.
Time of gas flow, 10 mim.

several factors have been taken up and studied.

The Flotation of Ferric Ions by ODAC.—*The Effect of the Ferric Ion Concentration.*—Figure 2 shows the effect of the ferric ion concentration upon the flotation efficiency, R, for the Fe^{3+}-EDTA-ODAC system at constant ODAC and EDTA concentrations, and at a constant rate and time (10 min.) of gas-flow. It may be seen that R increased from 16 to 160 with the decrease in the ferric sulfate concentration from 7×10^{-5} mol./l. to 7×10^{-6} mol./l. This is in accord with the general trend of ion flotation.[3] By 10 mins' gas flowing, about 54% of the ferric ions in 50 cc. of the 7×10^{-6} mol./l. initial solution was removed and concentrated in about 0.17 cc. of foam.

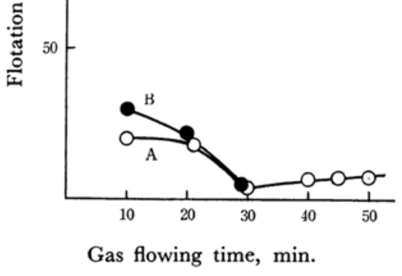

Fig. 3. Flotation efficiency vs. gas flowing time for Fe^{3+}-EDTA-ODAC system.
ODAC, 3.16×10^{-4} mol./l.; EDTA, 1.70×10^{-4} mol./l.; Fe^{3+} conc.: A, 6.4×10^{-4}; B, 6.8×10^{-4}; C, 5.0×10^{-6} mol./l.

The Effect of the Time of the Gas-Flow.—Figure 3 shows the relation between the time of gas-flow and R at constant concentrations of ODAC, EDTA and ferric ions. We can see in this figure that the overall (integrated) value of R decreased with the increase in the gas-flow time. Further, a marked increase in R with the dilution of ferric ions can be confirmed. The value of $R=150$ for 20 mins' gas flowing in a 5×10^{-6} mol./l. ferric sulfate solution corresponds to a complete removal of ferric ions from the solution by foaming. These facts again agree with the general tendency of the ion flotation.[3]

The Effect of the Collector Concentration.—Figure 4 shows the effect of the collector concentration of R when the rest of the conditions were held constant. As may be seen in this figure, the effect of the EDTA concentration is not very distinct at 10 mins' gas flowing, while the increase in R can be confirmed with increasing concentrations of EDTA at 30 mins' gas flowing. Here, it should be noticed that no small value of R is confirmed even when the concentration of EDTA is zero. This is rather unexpected, since it is a case of cation flotation by a cationic surfactant, just the opposite of the usual case of ion flotation by an oppositely charged surfactant. This will be discussed in detail in a later section.

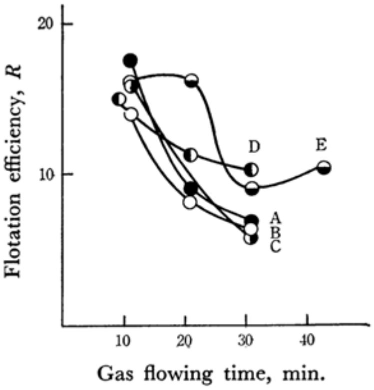

Fig. 4. Flotation efficiency vs. gas flowing time for Fe^{3+}-EDTA-ODAC system.
ODAC 3.3×10^{-4} mol./l., Fe^{3+} 6.4×10^{-5} mol./l.
EDTA A 0, B 3.6×10^{-6}, C 7.2×10^{-6}, D 3.6×10^{-5}, E 1.7×10 mol./l.

The Effect of the Surfactant Concentration.—Since the existence of EDTA did not seem to be essential, measurements were made for the effect of the surfactant concentration on the flotation of ferric

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[3] H. Schoen and G. Gazzella, *Industrial Water Wastes*, May—June, 71 (1961).

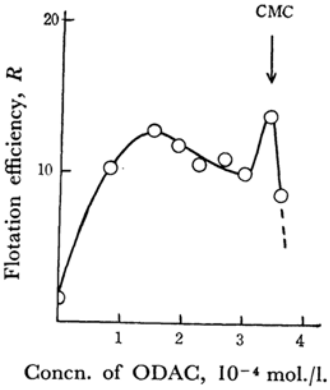

Fig. 5. Flotation efficiency vs. ODCA concn. for Fe^{3+}-ODAC system.
Time of gas flowing, 10 min.; Fe^{3+}, 6.4×10^{-5} mol./l.

ions from the solution without the addition of EDTA. The results are shown in Fig. 5. We can see in this figure that R does not change appreciably over a wide range of ODAC concentration, except for a zero concentration, and presumably beyond the critical micelle concentration, where R steeply falls to a small value. In the case of the measurement at a zero concentration of ODAC, a flotation cell as is shown in Fig. 1B was used, since the foam produced was very unstable. This cell separated the surface zone of the solution from its bulk by a diaphragm with a small opening in its center which allowed the passage of bubbles. The bubbles bursted on the surface of the solution, leaving the surface layer rich in the solute, which was then prevented from mixing with the interior of the solution. After the gas had flowed, the surface layer was taken for the determination of the concentration, and the R value was calculated. Thus the value of 1.5 was obtained. Strictly speaking, the value obtained here cannot be plotted on the same scale as those obtained by the former method, but it may be used for the purpose of comparison with other data as a whole.

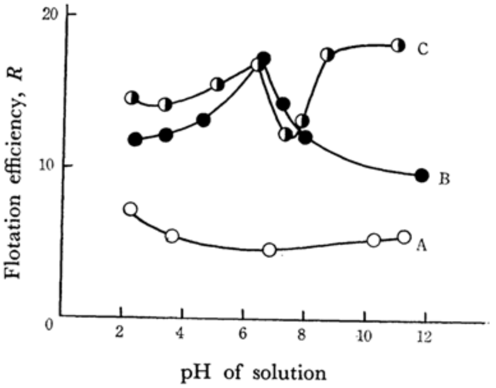

Fig. 6. Flotation efficiency vs. pH for Fe^{3+}-EDTA-ODAC, Fe^{3+}-EDTA and Fe^{3+}-ODAC system.
A: EDTA, 1.0×10^{-4}mol./l.; Fe^{3+}, 6.4×10^{-5}mol./l.
B: ODAC, 2.99×10^{-4}mol./l.; Fe^{3+}, 6.4×10^{-5}mol./l.
C: ODAC, 3.02×10^{-4}mol./l.; EDTA, 1.0×10^{-4}mol./l.; Fe^{3+} 6.4×10^{-5} mol./l.

The Effect of the pH.—In all the above experiments, the pH of the solution was not especially controlled: it was about 4. Now, aqueous ferric sulfate solutions containing ODAC and/or EDTA varying in pH value were studied. The results are shown in Fig. 6. In this experiment, the pH of the solution was controlled by using hydrochloric acid and sodium hydroxide.
The measurement of the R value for the Fe^{3+}-EDTA system was made by using the apparatus shown in Fig. 1B.

It may be seen in Fig. 6 that the systems containing both EDTA and ODAC show R values larger than those containing ODAC alone in the regions of pH higher than about 8 and lower than 6. Between pH 6 and 8, the difference in R value between both systems is not distinct. The latter system shows a maximum R value at about pH 6. This maximum may be explained as the optimum pH region of the formation of a coordination compound consisting of ferric ions and free octadecyldimethylamine, as was pointed out by Sebba.[4] The system containing EDTA alone shows a smaller value of R than these two systems, though the comparison is somewhat qualitative in this case.

Let us now attempt to explain the change in flotation efficiency with the pH value for the Fe^{3+}-EDTA-ODAC system. It can readily be seen from the coincidence of the maximum of R between the Fe^{3+}-ODAC system and the Fe^{3+}-EDTA-ODAC system in Fig. 6, that the flotation of Fe in the latter system near pH 6 is mainly due to the formation of the Fe^{3+}-ODAC complex, while the flotation of Fe in a low pH region is considered to be due to the formation of both Fe^{3+}-ODAC and Fe^{3+}-EDTA complexes, as is expected from the R values of these systems. As for the explanation of the large increase in R for the Fe^{3+}-EDTA-ODAC system in an alkaline region, the flotation of Fe by Fe^{3+}-ODAC and Fe^{3+}-EDTA interaction seems insufficient. Here, we may conceivably take account of Fe^{3+}-EDTA-ODAC linkage, since the interaction between EDTA and ODAC is expected to show a broad optimum in an alkaline region, considering the rather strongly basic nature of ODAC.

Thus, we can explain the total flotation effect of Fe over a wide range of pH by the above three interactions of Fe^{3+}-ODAC, Fe^{3+}-EDTA and Fe^{3+}-EDTA-ODAC. The so-called sublate salt formation insisted on by Sebba[4] is not marked in this system, since the interaction between Fe

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[4] F. Sebba, "Ion Flotation," Elsevier Publisher, London, New York (1962), p. 71.

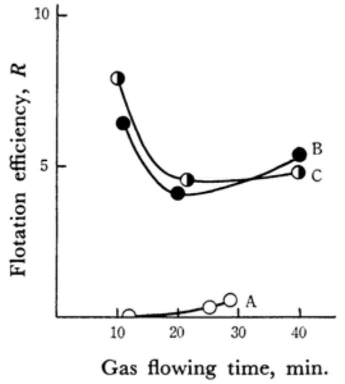

Fig. 7. Flotation efficiency vs. gas flowing time for Fe^{3+}-SDS system.
SDS: 3.0×10^{-3} mol./l.
Fe^{3+}: A, 1.7×10^{-5} mol./l.; B, 6.1×10^{-5} mol./l.; C, 1.8×10^{-4} mol./l.

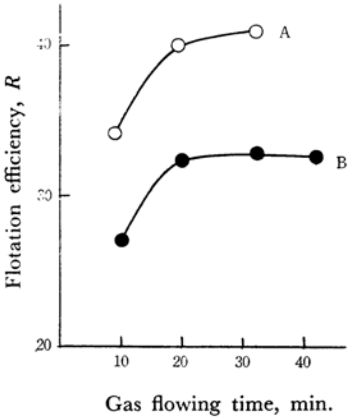

Fig. 8. Flotation efficiency vs. gas flowing time for Fe^{2+}-SDS system.
A: SDS, 2.99×10^{-3}mol./l.; Fe^{2+}, 1.58×10^{-4}mol./l.
B: SDS, 3.10×10^{-3}mol./l.; Fe^{2+}, 2.58×10^{-4}mol./l.

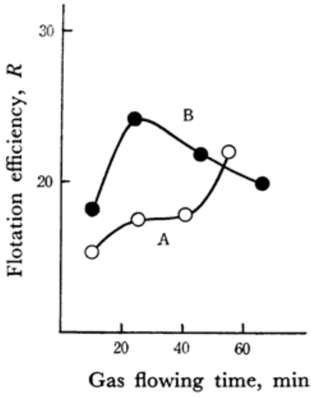

Fig. 9. Flotation efficiency vs. gas flowing time for Ag^+-SDS and Malachite Green ion - SDS systems.
A: SDS, 3.03×10^{-3}mol./l.; Ag^+, 6.7×10^{-5}mol./l.
B: SDS, 5.69×10^{-3}mol./l.;
Malachite Green ion, 1.8×10^{-5} mol./l.

and the surfactant is rather weak in a low pH region, contrary to his case. A slight increase in R in the acid region may be due to the formation of a simple compound of Fe^{3+}-ODAC, together with Fe^{3+}-EDTA, as has been mentioned above. The co-operating action of ODAC and EDTA in the flotation, especially in the alkaline region, would correspond to the action of polyaminopolycarboxylic acid, which is known to be effective in ion flotation.[5] This may suggest that the functional radicals of the collecting and frothing actions need not coexist in a single molecule, but that they can exist in separate molecules in a mixed solution, to show an effective ion flotation. This would open many possibilities in the practice of the choice of flotation agents.

The Flotation of Ferric, Ferrous, Silver and Malachite Green Ions by SDS.—The effect of the gas-flow-time on aqueous Fe^{3+}-SDS, Fe^{2+}-SDS, Ag^+-SDS and Malachite Green - SDS systems is shown in Figs. 7, 8 and 9. It may be seen in these figures that the values of R do not decrease, but rather increase, with time, except for the case of Fe^{3+}-SDS, which exhibits a decrease similar to that of the Fe^{3+}-ODAC system (cf. Fig. 4). This increase may come from the relatively insoluble nature of the corresponding SDS salts, the flotation of which is largely independent of the concentration of the cation to be floated. The increase in R with the gas-flow time is especially marked in the case of the Ag^+-SDS system, which forms an insoluble salt and an unstable foam. The effect of the concentration of the cation to be floated upon R was examined for ferric and ferrous ions, as may be seen in Figs. 7 and 8. The

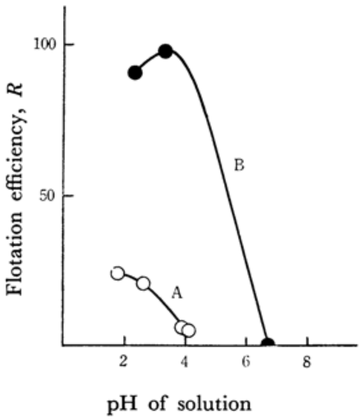

Fig. 10. Flotation efficiency vs. pH for Fe^{3+}-SDS and Fe^{2+}-SDS systems.
A: gas flowing time, 20 min.
SDS, 3.00×10^{-3} mol./l.; Fe^{3+}, 7.5×10^{-5} mol./l.
B: gas flowing time, 10 min.
SDS, 2.99×10^{-3} mol./l.; Fe^{2+}, 3.2×10^{-5} mol./l.

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[5] R. W. Schnepf, E. L. Garden, Jr., E. Y. Mirocznik and E. Schonfeld, *Chem. Eng. Prog.*, **55**, 42 (1959).

results were somewhat irregular for ferric ions, but a trend similar to that in the case of the Fe^{3+}-EDTA-ODAC system was seen for ferrous ions.

The effects of the pH on Fe^{3+}-SDS and Fe^{3+}-SDS systems are shown in Fig. 10. The values of R for both systems are large in the region of low pH, but they decrease rapidly with an increase in the pH value, reaching zero near pH 4—5 in the former system and near pH 7 in the latter system. This fact was also inferred by Sebba.[6] It may be explained by the lower solubility of ferric than that of ferrous hydroxide. In fact, in the solutions near the above pH's, white precipitates appeared and the foam became very unstable.

The authors wish to express their thanks to Mr. M. Nakamura of our laboratory for his assistance in this work. They also thank the Ministry of Education for the Scientific Research Expenditure Grant given to facilitate the present work.

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[6] Ref. 4, p. 109.