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Macromolecular Ion Flotation of Fe^{3+}, Cu^{2+}, and Ni^{2+} Ions by Combined Use of Macromolecular Anions and Cationic Surfactant

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Macromolecular ion flotation of Fe^{3+}, Cu^{2+}, and Ni^{2+} ions was studied using macromolecular ions such as sodium metasilicate, sodium polyacrylate, sodium carboxymethylcellulose, sodium alginate, and sodium cyclo-hexaphosphate (SCHP) together with hexadecyltrimethylammonium chloride (HTAC). Diagrams of floatability *vs.* composition of macromolecular ion and HTAC, and floatability *vs.* pH at fixed composition of macromolecular ions and HTAC were constructed. Regions of optimum composition and pH for the flotation were determined and tabulated. Maximum floatabilities greater than 95%, some attaining nearly 100%, in the alkaline region were obtained for most of the systems, except for the system Fe^{3+}–SCHP–HTAC which showed its maximum floatability, 91.7%, in the acid region. Metallic ions are considered to be combined as hydroxides with macromolecules which are then floated.

In a previous paper,[1)] we have reported the flotation of Fe^{3+} and MnO_4^- ions by sodium metasilicate and cationic surfactant and the flotation of MnO_4^- ions by many other macromolecular anions, including macroscopic or colloidal particles possessing ion exchange capacity and organic or inorganic polymer ions together with cationic surfactant.[2)] The present paper reports the macormolecular ion flotation of Fe^{3+}, Cu^{2+}, and Ni^{2+} ions by various macromolecular anions, such as sodium polyacrylate (SPA), sodium alginate (SAlg), sodium carboxymethylcellulose (SCMC), sodium metasilicate (SMS), and sodium cyclo-hexaphosphate (SCHP) together with cationic surfactant, hexadecyltrimethylammonium chloride (HTAC).

Experimental

Materials. SPA was commercial pure product of polymerization degree 22000—66000. SAlg was a product of commercial pure grade. Its 0.3% aqueous solution showed relative viscosity to water of 12.5 at 30 °C. SMS, SCHP, and SCMC were commercial products of guaranteed grade. HTAC was a product of commercial pure grade. These reagents were kept in a desiccator and used without further purification. Iron(III) chloride, coppor(II) sulfate, and nickel(II) sulfate of guaranteed grade were used as cations to be floated.

Measurement. For the flotation measurement, 20 cm^3 of a solution containing ions to be floated, macromolecular ions, HTAC and HCl or NH_3 if necessary for controlling pH was introduced in a stoppered test tube of 16 mm in inner diameter and 290 mm in length equipped with a stopcock at the bottom. The test tube was slowly moved upside down for 2 min, then vigorously shaken 20 times by hand. After being kept for 10 min to complete flotation, concentrations of Fe^{3+}, Cu^{2+}, and Ni^{2+} ions in the underlying solution were measured and the floatability percent, F, was calculated by the following equation:

$$F = \frac{C_i - C_f}{C_i} \times 100\%,$$

where C_i and C_f denote concentrations of the ions to be floated in the solution before and after the flotation, respectively.

The concentrations of Fe^{3+}, Cu^{2+}, and Ni^{2+} ions were measured with a Hitachi Atomic Absorption Spectrometer 508 at wave lengths 248.3, 324.7, and 232 nm, respectively.

The measurement of flotation was carried out at room temperature, about 25 °C.

Results and Discussion

Flotation by SPA. *Flotation of Fe^{3+} Ions*: Figure 1 shows the floatability of Fe^{3+} ions as a function of total concentration of SPA+HTAC and weight fraction of SPA/(SPA+HTAC) at pH about 8.2. The concentra-

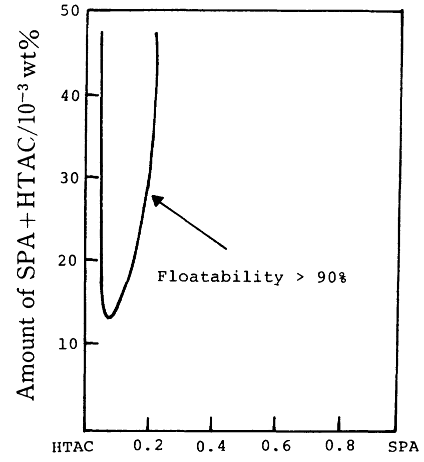

Fig. 1. Diagram of Fe^{3+} ion flotation by SPA and HTAC. F^{3+}: 1.98×10^{-4} mol dm^{-3}, pH: 8.2.

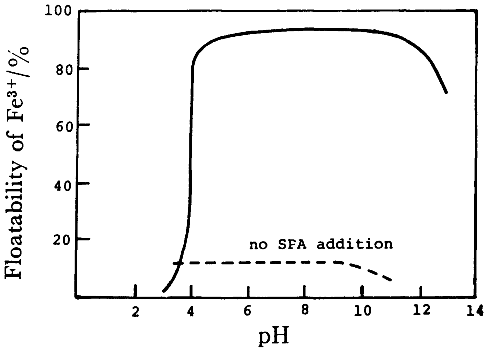

Fig. 2. Floatability of Fe^{3+} ion *vs.* initial pH for SPA+HTAC system.
Fe^{3+}: 1.93×10^{-4} mol dm^{-3}, SPA: 1.5×10^{-3} wt%, HTAC: 3.1×10^{-3} wt%.

tion of Fe^{3+} ions was kept constant at 1.92×10^{-4} mol dm^{-3}. The area inside the curve shows the optimum region of Fe^{3+} ion flotation, more than 90% floatability. Maximum floatability of 93.8% was obtained at 31×10^{-3} wt% SPA and 1.86×10^{-3} wt% HTAC.

Figure 2 shows the pH dependence of floatability of Fe^{3+} ions at the nearly maximum floatability condition of 1.9×10^{-4} mol dm^{-3} Fe^{3+}, 1.5×10^{-3} wt% SPA, and 28.8×10^{-3} wt% HTAC. As shown by the solid line, floatability became perceptible at about pH 3, sharply increased at pH 4, and gave a plateau of nearly 93% in pH range 5 to 11. Beyond pH 12, floatability sharply decreased. The beginning of the floatability increase at pH 3 is near the pH at which $Fe(OH)_3$ precipitation begins to form, as calculated from its solubility product and the concentration of Fe^{3+} ions used. It is confirmed that SPA effectively acts in the macromolecular ion flotation of Fe^{3+}, since the system without SPA exhibited only a slight floatability in this pH range as shown by the broken line in Fig. 2.

Flotation of Cu^{2+} Ions: Figures 3 and 4 show floatability *vs.* composition and floatability *vs.* pH relations for Cu^{2+}–SPA–HTAC system, corresponding to Figs. 1 and 2 for Fe^{3+} flotation, respectively. In Fig. 3, the concentration of Cu^{2+} ions was kept constant at 1.74×10^{-4} mol dm^{-3}, and pH at 9.8. The region of floatability more than 90% is indicated by a curve, the shape of which is different from that of Fig. 1 for Fe^{3+} ions; it forms a narrow vertical area resembling the case of the flotation of Fe^{3+} or MnO_4^- ions by SMS.[1)]

The pH dependence of the floatability of Cu^{2+} ions is shown in Fig. 4, where concentrations of Cu^{2+} ions, SPA, and HTAC were 1.79×10^{-4} mol dm^{-3}, 4.1×10^{-3} wt%, and 15.5×10^{-3} wt%, respectively. Floatability sharply rose from about pH 6, showed a flat maximum of nearly 96% in pH range 7 to 9 and decreased to nearly zero beyond pH 10, as shown by the solid line. The sharp rise of floatability at pH 6 is close to the pH of the beginning of $Cu(OH)_2$ precipitate formation as calculated from its solubility product and Cu^{2+} ion concentration. Again, the addition of SPA is found effective for Cu^{2+} ion flotation, as is evident from the comparison of solid line with the floatability curve of the system without the addition of SPA, as shown by the broken line in Fig. 4.

Flotation by SAlg. *Flotations of Fe^{3+} and Cu^{2+} Ions*: Figures 5 and 6 show the floatability *vs.* composition and floatability *vs.* pH relations for the Fe^{3+}–SAlg–HTAC

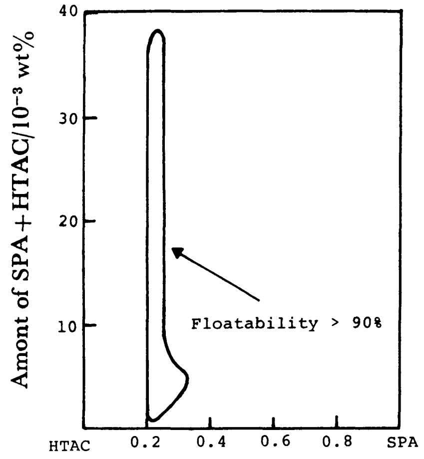

Fig. 3. Diagram of Cu^{2+} ion flotation by SPA and HTAC.
Cu^{2+}: 1.74×10^{-4} mol dm^{-3}, pH: 9.8.

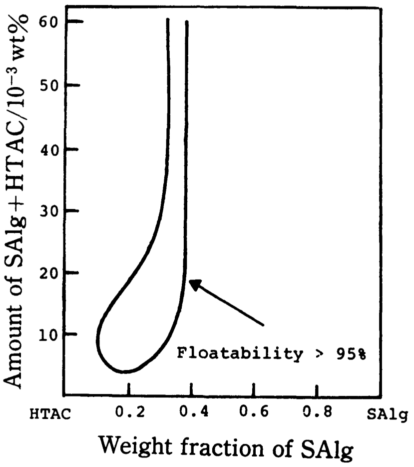

Fig. 5. Diagram of Fe^{3+} ion flotation by SAlg and HTAC.
Fe^{3+}: 1.80×10^{-4} mol dm^{-3}, pH: 9.0.

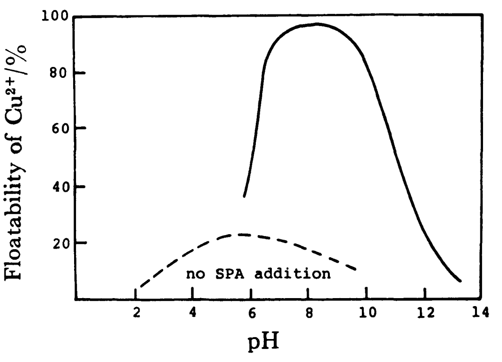

Fig. 4. Floatability of Cu^{2+} ion *vs.* initial pH for SPA+HTAC system.
Cu^{2+}: 1.79×10^{-4} mol dm^{-3}, SPA: 4.1×10^{-3} wt%, HTAC: 15.5×10^{-3} wt%.

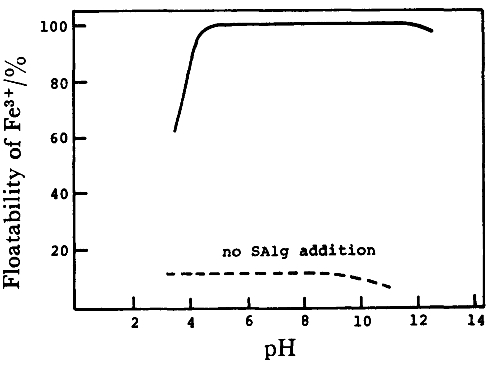

Fig. 6. Floatability of Fe^{3+} ion *vs.* initial pH for SAlg+HTAC system.
Fe^{3+}: 1.79×10^{-4} mol dm^{-3}, SAlg: 8.3×10^{-3} wt%, HTAC: 15.2×10^{-3} wt%.

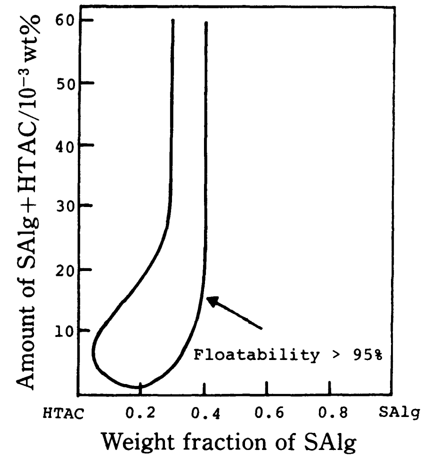

Fig. 7. Diagram of Cu^{2+} ion flotation by SAlg and HTAC.
Cu^{2+}: 1.81×10^{-4} mol dm^{-3}, pH: 9.1.

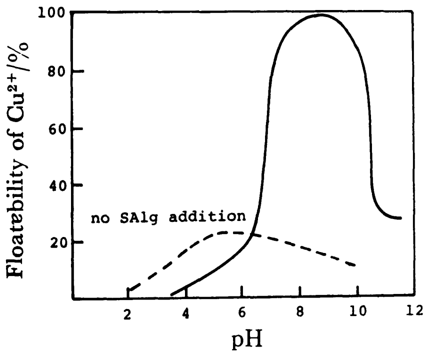

Fig. 8. Floatability of Cu^{2+} ion *vs.* initial pH.
Cu^{2+}: 1.74×10^{-4} mol dm^{-3}, SAlg: 8.2×10^{-3} wt%, HTAC: 15.6×10^{-3} wt%.

system. Figures 7 and 8 show similar relations for the Cu^{2+}–SAlg–HTAC system. Experimental conditions of Figs. 5 through 8 are listed in each figure caption. As shown in Figs. 5 and 7, and Figs. 6 and 8, the floatability behaviors of Fe^{3+} and Cu^{2+} ions for SAlg are similar as a whole to those for SPA. But in the former case, regions of optimum floatability more than 95% are shown in Figs. 5 and 7. The floatability of nearly 100% is seen in the pH region 5 to 12 for the Fe^{3+}–SAlg–HTAC system in Fig. 6. In the case of the Cu^{2+}–SAlg–HTAC system, a flat maximum of nearly 100% floatability is seen in the pH region 8 to 9 in Fig. 8. Figs. 6 and 8 also show the effectiveness of the addition of SAlg for the flotation of Fe^{3+} and Cu^{2+} ions as seen from the comparison of the solid line with the broken line in these figures.

Flotations of Fe^{3+}, Cu^{2+}, and Ni^{2+} Ions by Other Macromolecular Anions. Flotations of Fe^{3+}, Cu^{2+}, and Ni^{2+} were carried out using SMS, SCMC, and SHMP as macromolecular or polymer ions and HTAC as frother. Similar diagrams of floatability *vs.* composition and floatability *vs.* pH were obtained, which are not shown. Instead, the best conditions of flotation for these systems together with those for SPA and SAlg are shown in

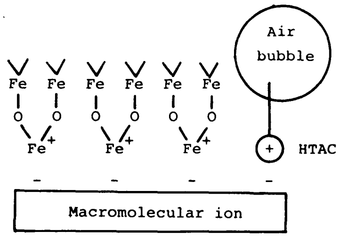

Fig. 9. Sublate structure consisting of macromolecular ion and Fe^{3+} ion.

Table 1. Macromolecular ion flotation of Fe^{3+}, Cu^{2+}, and Ni^{2+}

Ion	Concn of ion / 10^{-4} mol dm^{-3}	Concn of HTAC / wt%	Concn of SMS / wt%[a]	pH	*F*/%
Fe^{3+}	1.73	0.024	0.075	11.7	97.3
Cu^{2+}	1.82	0.0061	0.078	12.0	96.4
Ni^{2+}	1.72	0.0138	0.173	11.6	97.3
			Concn of SPA / wt%	pH[b]	
Fe^{3+}	1.93	0.0186	0.0031	8.2	93.8
Cu^{2+}	1.74	0.0153	0.0052	9.8	98.0
			Concn of SCMC / wt%	pH[b]	
Fe^{3+}	1.73	0.020	0.0139	9.1	98.4
Cu^{2+}	1.79	0.0153	0.0100	9.5	99.2
			Concn of SAlg / wt%	pH[b]	
Fe^{3+}	1.80	0.0182	0.0082	9.0	99.0
Cu^{2+}	1.81	0.0622	0.0005	9.1	98.6
			Concn of SCHP / wt%	pH[c]	
Fe^{3+}	1.77	0.0548	0.0327	1.8	91.7

a) Addition of 0.0008 wt% SPA. b) Addition of NH_3. c) Addition of HCl.

Table 1.

The floatabilities are 97 to 99% for most systems in the alkaline region, except for the Fe^{3+}–SCHP–HTAC system, which gave a maximum floatability of 91% at pH 1.7.

The tentative molecular model of the sublate containing metallic ions, for instance Fe^{3+} ions, is indicated in Fig. 9, except for the Fe^{3+}–SCHP–HTAC system. This model is the generalized reproduction of what has been proposed in the previous paper.$^{1)}$ In Fig. 9, macromolecular anions take up both HTAC and metallic cations, and HTAC catches bubbles. The metallic ions are presumably in the state of large metallic hydroxide aggregates carrying a few residual positive charges. In the case of the Fe^{3+}–SCHP–HTAC system, simple Fe^{3+} ions are considered to combine with cyclo-hexaphosphate ions. Thus macromolecular ions or polymer ions in general are confirmed to be effective for the flotation of metallic cations such as Fe^{3+}, Cu^{2+}, and Ni^{2+} ions, as well as for the flotation of MnO_4^- ions already reported.$^{1)}$

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