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The Macromolecular Ion Flotation of Fe^{3+}, Cu^{2+}, and Ni^{2+} by the Use of Charcoal and Cationic Surfactant

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The macromolecular ion flotation of Fe^{3+}, Cu^{2+}, and Ni^{2+} ions by the combined use of charcoal and hexadecyltrimethylammonium chloride (HTAC) was studied. The flotation of powdered active charcoal itself was first studied; a 100% floatability was obtained for the flotation of 2500 ppm charcoal by the addition of 6 ppm of polyacrylamide and 550 ppm of HTAC in the pH range from 4 to 13. For the studies of the flotation of Fe^{3+}, Cu^{2+}, and Ni^{2+} ions, diagrams of the floatability of the respective ions *vs.* the composition of charcoal and HTAC, and the floatability of the respective ions *vs.* the pH at a constant composition of charcoal and HTAC, were constructed. A nearly 100% floatability was obtained for Fe^{3+}, Cu^{2+}, and Ni^{2+} ions at pH values larger than 4.5, 9.5, and 11 respectively. This order is the same as that of the solubility products of $Fe(OH)_3$, $Cu(OH)_2$, and $Ni(OH)_2$. It was confirmed that Fe^{3+} ions are adsorbed as hydroxides on charcoal; they are subsequently floated over the whole range of pH values combined with charcoal, while the Cu^{2+} and Ni^{2+} ions are adsorbed as simple ions on charcoal and floated in the lower pH region. They are adsorbed as hydroxide on charcoal and floated in a higher pH region.

In preceding papers, we have reported the applicability of macromolecular ion flotation to the flotation of inorganic and organic anions and cations.[1,2] There, macromolecular ions, namely, macroscopic or colloidal particles possessing an ion-exchange capacity and organic or inorganic polymer ions, together with ionic surfactants with an electric charge the opposite of that of macromolecular ions, were used.

To date, ion flotation using charcoal and surfactant has not been reported, although flotations of charcoal by surfactants have been reported.[3,4] Considering the remarkable adsorbing power of charcoal for various organic and inorganic ions, effective ion flotation by the use of charcoal can be expected.

In this case, powdered active charcoal is preferable, since this offers both a very large and readily accessible area for the substance to be floated. However, the powdered charcoal has the difficulty of not being easily floated.[4] In the present paper, this difficulty could be overcome by the addition of a small amount of polyacrylamide.

In the present paper, charcoal was used as the macromolecular ion in our series of studies.[1] Fe^{3+}, Cu^{2+}, and Ni^{2+} ions were floated by HTAC.

Experimental

Materials. The charcoal was the product of Wako Pure Chemicals, labelled "Chemical Activated." HTAC was the product of Wako Pure Chemicals of a chemically pure grade. The polyacrylamide DCLE MA-3000H (PAA) was the product of Mitsubishi Chemical Industries, the mean degree of polymerization being 1×10^5. The $FeCl_3$, $CuSO_4$, and $NiSO_4$ were commercial products of a guaranteed grade.

Measurement. For the flotation measurement, 20 cm^3 of a solution containing the ions to be floated, charcoal, HTAC, and HCl or NaOH if necessary for controlling the pH was introduced into a stoppered test tube 16 mm in inner diameter and 290 mm in length, equipped with a stopcock at the bottom. The test tube was shaken 20 times by hand. After the test tube had been kept standing for 10 min to complete the flotation, the concentrations of Fe^{3+}, Cu^{2+}, and Ni^{2+} ions in the underlying solution were measured and the floatability percentage, *F*, was calculated by means of the following equation:

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

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

The concentrations of the Fe^{3+}, Cu^{2+}, and Ni^{2+} ions were measured with a Hitachi Atomic Absorption Spectrometer 508 at wave lengths of 248.3, 324.7, and 232 nm respectively.[2] The pH was controlled if necessary by the addition of HCl or, NaOH.

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

Results and Discussion

Floatability of Charcoal. First, we studied the floatability of charcoal. The floatability of charcoal *vs.* the concentration of the PAA relation was studied at constant concentrations of 2500 ppm of charcoal and 550 ppm of HTAC at pH 4.0. The floatability increased from zero at zero ppm of PAA to 100% at 4.5 ppm of PAA, beyond which it remained constant. Therefore, we fixed the concentration of PAA at 6 ppm and examined the relation between the concentration of HTAC and the floatability of charcoal at pH 6. The solid line of Fig. 1 shows the result. It can be confirmed

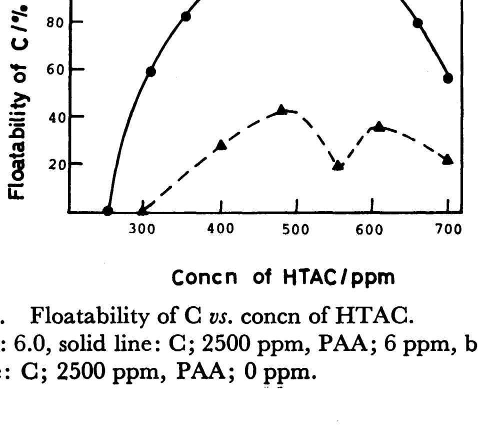

Fig. 1. Floatability of C *vs.* concn of HTAC.
pH: 6.0, solid line: C; 2500 ppm, PAA; 6 ppm, broken line: C; 2500 ppm, PAA; 0 ppm.

that a flat maximum of a nearly 100% floatability could be obtained in the concentration region from 400 to 600 ppm HTAC. In the same figure, the charcoal–HTAC system without the addition of PAA is shown by a broken line. The effectiveness of the addition of PAA is evident for charcoal flotation.

We further measured the floatability of charcoal *vs.* the pH relation at constant concentrations of 2500 ppm of charcoal, 6 ppm of PAA, and 550 ppm of HTAC, as shown in Fig. 2. A broad maximum of a nearly 100% floatability of charcoal was obtained in the pH region from 4 to 13. The system without PAA is shown by a broken line in Fig. 2. We can see a similar floating effect of the addition of PAA.

Floatability of Fe^{3+}, Cu^{2+}, and Ni^{2+} vs. *Composition of PAA and HTAC.* Macromolecular ion flotations of Fe^{3+}, Cu^{2+}, and Ni^{2+} were carried out with the addition of 2500 ppm of charcoal, 6 ppm of PAA, and varying compositions and total amounts of charcoal and HTAC. Figure 3 shows the floatabilities of the Fe^{3+}, Cu^{2+}, and Ni^{2+} ions as a function of the total weight concentration of C† + HTAC and the weight fraction of C/(C+HTAC) at pH 10.8, 10.0, and 11.1 respectively. The concentration of Fe^{3+}, Cu^{2+}, and Ni^{2+} were kept constant at 1.65×10^{-4}, 1.83×10^{-4}, and 1.69×10^{-4} mol dm^{-3} respectively. The areas inside the curves indicate the optimum composition regions of floatability larger than 95%. The upper parts of these optimum regions form a vertical shape, while the lower parts bend towards 100% HTAC.

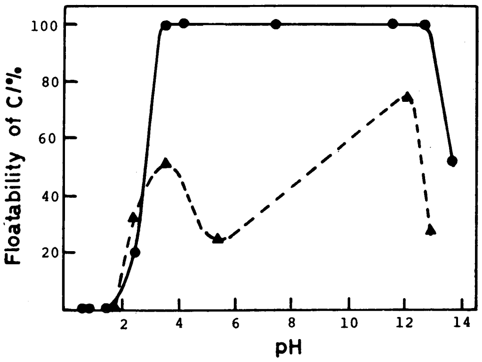

Fig. 2. Floatability of C *vs.* pH.
Solid line: C; 2500 ppm, PAA; 6 ppm, HTAC; 550 ppm, broken line: C; 2500 ppm, PAA; 0 ppm, HTAC; 550 ppm.

Floatabilities of Fe^{3+}, Cu^{2+}, and Ni^{2+} vs. *pH.* The relations between floatabilities of Fe^{3+}, Cu^{2+}, and Ni^{2+} ions and pH were also measured; they are shown in Fig. 4. The experimental conditions are listed as a caption in the figure. In this figure, both the system with and that without the addition of charcoal are shown. In Fig. 4(a), showing the flotation of Fe^{3+} ions, the floatability sharply rose from zero to nearly 100% at pH 4, beyond which it remained constant up to pH 11. The effect of the addition of charcoal is evident from a comparison of this curve with the curve of the broken line without the addition of charcoal. In Fig. 4(b), showing the flotation of Cu^{2+}, the floatability gradually rose from zero at a pH of about 3 and attained nearly 100% beyond pH 9.4. The effect of the addition of charcoal is evident from a comparison of the curves of the solid and broken lines. In Fig. 4(c), showing the flotation of Ni^{2+}, the floatability rose gradually from zero at pH 3 and attained nearly 100% beyond a pH of about 11. The effect of the addition of charcoal can still be observed from a comparison of the solid and broken lines.

The values of the pH's at which Fe(OH)$_3$, Cu(OH)$_2$, and Ni(OH)$_2$ begin to form are calculated from each solubility product to be 2.2, 6.2, and 7.0 respectively. Considering these values, it is likely that Fe^{3+} ions are adsorbed as hydroxide on charcoal and that they are subsequently floated, while in the case of Cu^{2+} and Ni^{2+}, each ion is adsorbed on charcoal and floated in the low-pH region. In the high-pH region, however, the latter two hydroxides are considered to be adsorbed on charcoal and floated. The pH's beyond which the floatability remains at its maximum value for these ions

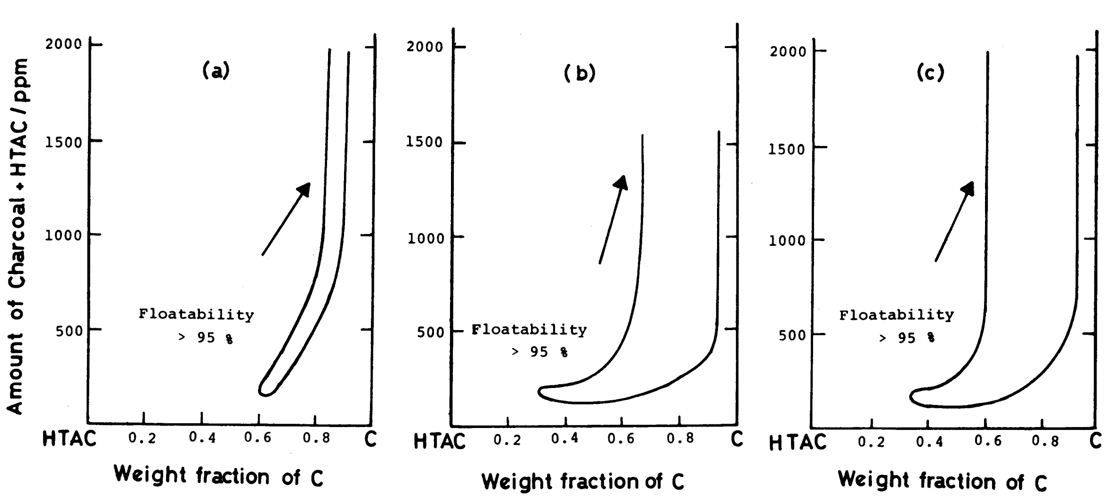

Fig. 3. Diagrams of Fe^{3+}, Cu^{2+}, and Ni^{2+} ion flotation by C, PAA and HTAC.
PAA: 6 ppm, (a): Fe^{3+} ion flotation, pH; 10.8, (b): Cu^{2+} ion flotation, pH; 10.0, (c): Ni^{2+} ion flotation, pH; 11.1.

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† Abbreviation of charcoal.

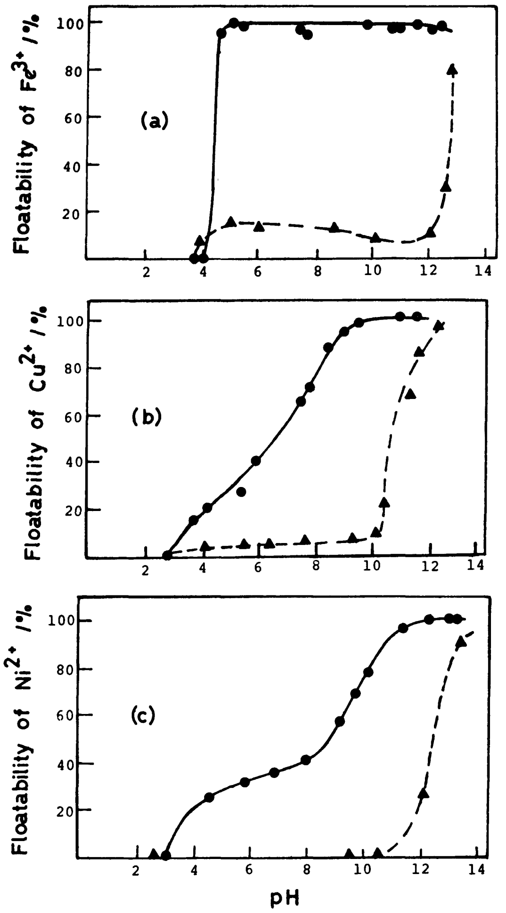

Fig. 4. Floatabilities of Fe^{3+}, Cu^{2+}, and Ni^{2+} ions *vs.* initial pH.
(a): Fe^{3+}; initial concn 1.67×10^{-4} mol dm^{-3}, (b): Cu^{2+}; initial concn 1.76×10^{-4} mol dm^{-3}, (c): Ni^{2+}; initial concn 1.69×10^{-4} mol dm^{-3}.
Solid line: C; 2500 ppm, PAA; 6 ppm, HTAC; 550 ppm, broken line: C; 0 ppm, PAA; 6 ppm, HTAC; 550 ppm.

are found to be:

$$Fe^{3+} < Cu^{2+} < Ni^{2+},$$

which is in the same order as that of the solubility product. A sharp rise in the floatabilities of these ions in the system without the addition of charcoal observed at a high pH may be explained by the sufficiently large hydroxide particle formed at a high pH being entangled in the foam.

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