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Flotation of MnO_4^- and Fe^{3+} Ions by the Combined Use of Sodium Silicate and Cationic Surfactant

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The removals of MnO_4^- and Fe^{3+} ions from an aqueous solution by the combined use of silicate ions(SiO_3^{2-}) and a cationic surfactant, hexadecyltrimethylammonium chloride (HTAC), were studied by means of ion flotation techniques. The effect of variables such as pH, the surfactant concentration, and the order of addition of the reagents on the floatability of the ions were studied. More than 98 and 97% of the MnO_4^- and Fe^{3+} ions, respectively, could be floated under the optimum conditions. The optimum composition of SiO_3^{2-} and HTAC was found to be about 0.9 in mole fraction of SiO_3^{2-} for both systems. It was also found that the order of the addition of the reagents markedly affects the floatability. Further, a schematic model of flotation was proposed, taking account of the compositions of the sublate. MnO_4^- and Fe^{3+} ion flotations differed from each other in that MnO_4^- ions combine with SiO_3^{2-} ions through the double layer of HTAC molecules, which are subsequently coagulated and floated by HTAC, while Fe^{3+} ions or polynuclear Fe^{3+} ions combine directly with SiO_3^{2-} ions, which are subsequently coagulated and floated by HTAC.

Ion flotation has been employed for the removal of inorganic anions and cations from an aqueous solution. The process involves the formation of a surface-active complex by the addition of surface-active ions opposite in charge to the ions to be separated. The complex is then floated by means of gas bubbles introduced into the solution. Various studies have been made of the reagents available for flotation and of the mechanism of flotation.[1)] Among the possible processes of ion flotation, the use of a surfactant with or without a polyelectrolyte has been confirmed to be effective for the flotation of anions, cations, and particles.[2)] Goto and Izumi have reported the removal of heavy metal ions from an aqueous solution by using polyethylenepolyamine.[3)] Cu^{2+}, Cd^{2+}, and Co^{2+} ions have been more effectively removed from an aqueous solution by the combined use of macromolecular or polymer anions, such as bentonite, and cationic surfactants than by the simple use of an anionic surfactant.[4,5)] So far, no application of ion flotation has been made to the removal of cations and anions from an aqueous solution by the combined use of silicate ions and a cationic surfactant, which also belongs to this category.

The present study is intended to establish the feasibility of ion flotation for the removal of anions and cations such as Fe^{3+} and MnO_4^- ions from an aqueous solution by the combined use of silicate ions and a cationic surfactant, hexadecyltrimethylammonium chloride (HTAC).

Experimental

Materials. The concentrated solution of about 2×10^{-3} mol/l permanganate solution was prepared by dissolving extra-pure grade potassium permanganate into triply distilled water; the solution was stocked in a dark room. The concentration of permanganate ions was determined by the usual method of titrating with a standard solution of sodium oxalate.

The iron(III) chloride used was of analytical reagent grade $FeCl_3\cdot6H_2O$, and was purified before use by recrystallization. A stock solution of 7.45×10^{-3} mol/l concentration was prepared by dissolving iron(III) chloride in triply distilled water, with the addition of a small amount of sulfuric acid to make the solution of pH 1.4. The concentration of Fe^{3+} ions was determined with an atomic absorption spectrometer (Techtron Pty., Ltd., Model-AA-100), using an aqueous solution of Mohr's salt of known concentration as a standard.

The cationic surfactant used was of pure grade hexadecyltrimethylammonium chloride (HTAC) supplied by the Kao Soap Co., Ltd.; its aqueous solution was prepared by dissolving HTAC in triply distilled water. The solution was employed after diluting just before use. The solution of silicate ions (SiO_3^{2-}) was prepared by dissolving reagent grade water glass in triply distilled water. The sodium hydroxide used for controlling pH was of extra-pure reagent grade, and was purified by precipitation from its saturated solution.

All other chemicals were of analytical reagent grade unless otherwise specified and were used without further purification.

Procedure. *MnO_4^- Ion Flotation*: In a test tube 1.65 cm in inner diameter and 16.5 cm in length, 10 ml of water, a given amount of potassium permanganate solution, and varying amounts of HTAC and sodium silicate solutions were introduced; the volume was filled with water to a total of 12 ml. The test tube of the sample solution was allowed to stand for 2 min and was slowly and repeatedly turned upside down. Then the precipitates formed with MnO_4^- were shaken for 10 s by hand and were floated with minute bubbles. After 5 min, the underlying liquid was taken out of the test tube and was centrifuged to remove the remaining precipitates. The concentration of permanganate ions in the solution was determined by a colorimeter (Bausch and Lomb, Spectronic 20) at 720 nm.

The floatability (%) of MnO_4^- ions was given by

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

where C_i and C_f denote the initial and final concentrations of MnO_4^- ions, respectively.

The concentration of HTAC and SiO_3^{2-} in the solution was determined as follows.

HTAC Concentration: Five ml of the solution without the precipitate was taken in a flask and mixed with 0.1 ml of Bromophenol Blue solution as a color indicator (a mixture of

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0.08% Bromophenol Blue, 62.5% acetic acid, 10.25% Na_2SO_4, and 27.17% water). The solution was titrated with sodium octadecylsulfate solution in a water bath at 60 °C.[6] The amount of HTAC in the sublate was calculated from the difference in the amount of HTAC in the solution before and after the precipitate formation.

SiO_3^{2-} Concentration: The concentration of SiO_3^{2-} was colorimetrically determined by the color developed by the addition of ammonium molybdate.[7] The absorbance was measured at 830 nm and the amount of SiO_3^{2-} in the sublate was calculated similarly to that of HTAC mentioned above. In some cases, the amount of SiO_3^{2-} in the sublate could not be determined as a difference owing to its small content. In such a case the sublate was removed and washed with distilled water, subjected to combustion in a platinum crucibles, fused with anhydrous sodium carbonate, and dissolved in triply distilled water. The solution was adjusted to pH 2 with sulfuric acid, and the amount of SiO_3^{2-} in the solution was determined by the colorimetry.

Fe^{3+} Ion Flotation. The varying amounts of Fe^{3+}, HTAC, and SiO_3^{2-} solutions and a small amount of sodium hydroxide solution were introduced into a graduated test tube 1.0 cm in inner diameter and 17 cm in length. The total volume of the solution was increased with water to 10 ml. The solution was treated in the same manner as in the case of the MnO_4^- ion flotation. After the flotation, about 5 ml of the underlying solution was taken out of the test tube for the measurements of the pH, concentration of HTAC, SiO_3^{2-}, and Fe^{3+}, from which the floatability of Fe^{3+} and the composition of the sublate were calculated. The floatability of the Fe^{3+} ions was calculated similarly to that of MnO_4^-.

The measurements of the flotation were carried out at room temperature, about 25 °C.

Results and Discussion

MnO_4^- Ion Flotation. Figure 1 shows the floatability of MnO_4^- as a function of total molar concentration of Na_2SiO_3+HTAC and mole fraction of Na_2SiO_3 in the mixture at pH 11. The area circumscribed by the curve shows the optimum region of MnO_4^- flotation, where more than 85% of MnO_4^- is floated. The triangles show the systems of less than 85% floatability, while the circles and squares indicate the systems with floatabilities of 90 and 98%, respectively. As may be seen in Fig. 1, the mole fractions of SiO_3^{2-} in the sample solution fall in a narrow range from 0.86 to 0.94 in the region of optimum flotation. In the upper region neighboring this optimum region (system No. 6 for instance), the flotation is not so efficient, although the permanganate ions coagulate completely. In the region of excess HTAC, the solution becomes turbid and the floatability decreases. Table 1 lists the floatability (F), and the solution and sublate compositions of the representative systems No. 1, 2, and 3 in the optimum flotation region in Fig. 1. Among these systems, a maximum floatability of 98% was obtained for the No. 2 system. From Table 1, the mole ratios of SiO_3^{2-} to HTAC of the sublates are seen to be about 2 for the three systems, while the mole ratios of HTAC to MnO_4^- are about 15.9, 7.52, and 2.47 for systems No. 1, 2, and 3 respectively, these decrease with decreasing amount of the total concentration of SiO_3^{2-}+HTAC.

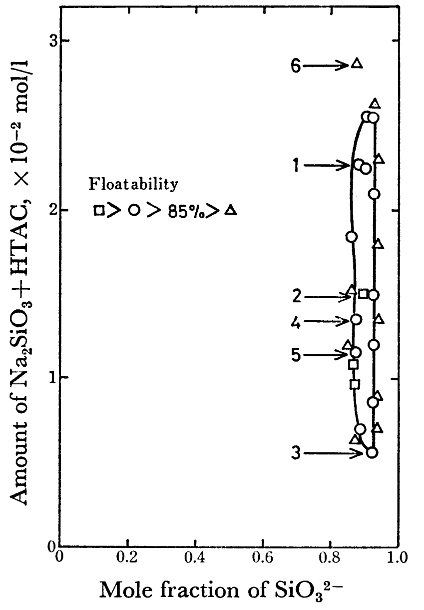

Fig. 1. Diagram of MnO_4^- ion flotation by SiO_3^{2-} and HTAC.

Table 1. Floatability of MnO_4^-, and solution and sublate compositions of the MnO_4^--SiO_3^{2-}-HTAC system

No.	F (%)	MnO_4^- (10^{-4} mol/l)[a]	HTAC (10^{-4} mol/l)	SiO_3^{2-} (10^{-4} mol/l)
1	85	1.91 (1.61)	26.3 (25.6)	200 (50.0)
2	98	2.01 (1.98)	15.7 (14.9)	137 (28.3)
3	91	2.08 (1.89)	4.92 (4.67)	54.0 (10.5)

( ) Indicates sublate compositions.

a) Mole number of each component in the sublate produced in 1 l solution.

In agreement with these data, some models of the sublate structure are proposed for these systems, as shown in Fig. 2.† In these models the double molecules bridging HTAC between MnO_4^- and SiO_3^{2-} are

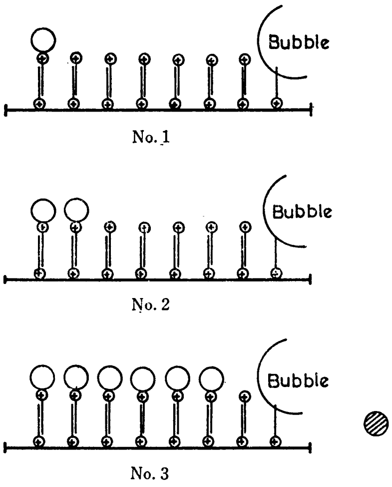

Fig. 2. A schematic drawing of sublate structure of MnO_4^--SiO_3^{2-}-HTAC precipitate. ├─┤: $(SiO_3^{2-})_n$, ○: combined MnO_4^-, ▨: free MnO_4^-, ⊕—: HTAC.

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† An exact agreement of the composition was not attempted, for the sake of simplicity.

indicated. HTAC also acts to float the sublates by attracting them to bubbles.

Now, in model No. 1, most MnO_4^- ions combine with silicate ions in the manner indicated in Fig. 2, but the excess positive charge due to the double molecular HTAC ions not combined with MnO_4^- increases the hydrophilicity and decreases the floatability. On the other hand, in model No. 3, nearly the full attachment of MnO_4^- ions is in equilibrium with some free MnO_4^- ions not attached to the silicate back-bone which does not float. Thus, the floatability of MnO_4^- again decreases. Therefore, a maximum of floatability is expected to appear somewhere between the two systems. System No. 2 may be considered to be such a system.

TABLE 2. FLOATABILITY OF MnO_4^- AND ORDER OF ADDITION OF REAGENTS

No.	F(%)	
	HTAC+SiO_3^{2-}	SiO_3^{2-}+HTAC
2	98	90
4	96	91
5	91.6	88

The effect of order of the addition of reagents on the floatability of MnO_4^- was also investigated. The results are shown in Table 2. As seen, the addition of SiO_3^{2-} to systems No. 2, 4, and 5 followed by HTAC shows less floatability than the addition of the reagents in the reverse order. This effect may be explained by the fact that HTAC combines mainly with SiO_3^{2-}, as is evidenced by the white precipitate of hexadecyltrimethylammonium silicate which forms, to which MnO_4^- attaches only weakly. Thus the floatability decreases in the fomer case, while in the latter case HTAC combines with both MnO_4^- and SiO_3^{2-}, enabling MnO_4^- to float by the double molecular bridge of HTAC.

Since in the case of MnO_4^- flotation we attempted merely to confirm the possibility of flotation of the anion by the polymer and surfactant addition, the pH of the solution (about 11) was not varied to study its effect on floatability.

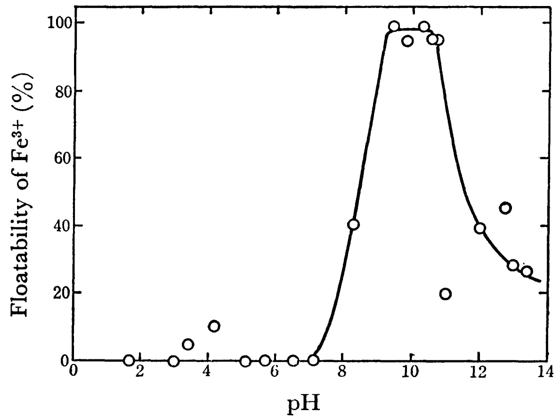


Fig. 3. Floatability *vs.* pH for Fe^{3+}–SiO_3^{2-}–HTAC system. Fe^{3+}: 7.45×10^{-5} mol/l, SiO_3^{2-}: 1.56×10^{-2} mol/l, HTAC: 2.02×10^{-3} mol/l.

Fe^{3+} Ion Flotation. In the case of Fe^{3+} ion flotation, as in the previous study,[8] the dissolved state of Fe^{3+} ions influencing the floatability was largely affected by the change in the pH, different from the case of MnO_4^-. Figure 3 shows the effect of the pH on the floatability for the Fe^{3+}–SiO_3^{2-}–HTAC system. As shown in Fig. 3, the floatability increases sharply at about pH 7 and reaches a maximum at a pH value from 9.4 to 10.7, showing an F of 97%. In the case of Fe^{3+} ion flotation by silicate ions and cationic surfactant, the Fe^{3+} ions directly combine with SiO_3^{2-}, which also combines with HTAC. At a pH value lower than 7, the floatability is practically zero for the Fe^{3+}–SiO_3^{2-}–HTAC system, presumably due to the strong adsorption of H^+ on the silicate back-bone with the exclusion of the adsorption of both Fe^{3+} and HTAC ions. In the case of Fe^{3+} ion flotation by an anionic surfactant alone and by bentonite and a cationic surfactant, the rise in floatability is seen at about pH 3 and above, as has been reported by Rubin and Johnson.[2,10] In the case of Fe^{3+} ion flotation, the iron polynuclear species forms at a certain pH, as has been reported by E. Matijevic *et al.*,[9] and then is floated by SiO_3^{2-} ions and HTAC.

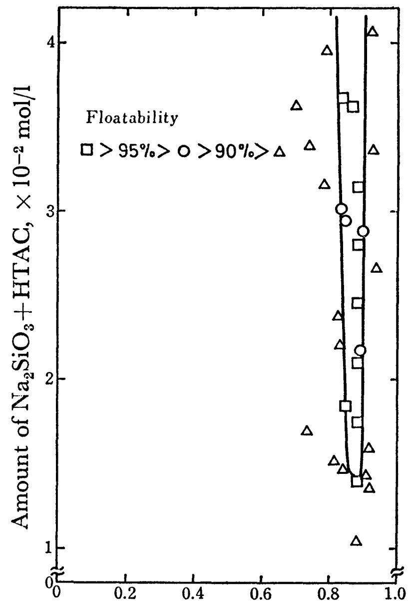


Fig. 4. Diagram of Fe^{3+} ion flotation by SiO_3^{2-} and HTAC.

Figure 4 shows the floatability diagram for Fe^{3+} at pH 9.4—10.7, similar to Fig. 1. The optimum region of Fe^{3+} ion flotation was observed in mole fractions of SiO_3^{2-} ranging from 0.85 to 0.90 and above the total concentration of 14.1×10^{-3} mol/l. In the region outside the optimum condition, the solution became turbid. In this solution the coagulation did not occur when the fraction of SiO_3^{2-} was smaller, while for a larger mole fraction of SiO_3^{2-}, it did occur, though the coagulate formed did not float. The diagram of Fig. 4 is quite similar to the case of MnO_4^-. Table 3 shows the optimum floatability and the compositions in mole of Fe^{3+}-sublate produced in 1 l solution, together with

Table 3. Sublate composition of the MnO_4^-–SiO_3^{2-}–HTAC and Fe^{3+}–SiO_3^{2-}–HTAC systems

F (%)	MnO_4^- (10^{-4} mol/l)$^{a)}$	Fe^{3+} (10^{-4} mol/l)	HTAC (10^{-3} mol/l)	SiO_3^{2-} (10^{-3} mol/l)
97.7		0.728	1.624	8.50
98.0	1.980		1.487	2.83

a) The same as mentioned in Table 1.

those of the MnO_4^--sublate. It is seen that the SiO_3^{2-}/HTAC ratios in the sublate at optimum floatability are about 5 for the Fe^{3+}–SiO_3^{2-}–HTAC system, as shown in Table 3, while the ratio is 2 for the MnO_4^-–SiO_3^{2-}–HTAC system. This difference can be expected, since in the former system Fe^{3+} ions combine directly with SiO_3^{2-} ions, while in the latter system cationic surfactant molecules act as bridges between MnO_4^- ions and SiO_3^{2-} ions. Figure 5 shows such a difference in the structures of the MnO_4^-–SiO_3^{2-}–HTAC and Fe^{3+}–SiO_3^{2-}–HTAC systems.

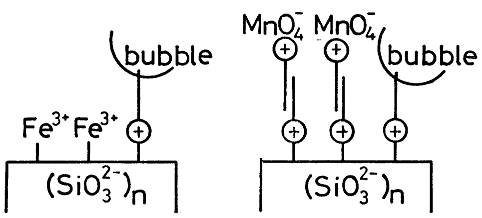


Fig. 5. Comparison of sublate structures of MnO_4^-–SiO_3^{2-}–HTAC and Fe^{3+}–SiO_3^{2-}–HTAC precipitates.

The flotation of Fe^{3+} ions was also carried out at higher Fe^{3+} concentrations near the optimum pH conditions. Thus, the effect of the order of addition of reagents upon the floatability could also be studied. The results are shown in Figs. 6, 7, and 8. As may be seen in Fig. 6, hardly any difference in the order of addition of regaents appears at the Fe^{3+} ion concentration of 6.68×10^{-5} mol/l, and the maximum floatability of 98% was obtained under the optimum conditions. In the more concentrated solution of 3.15×10^{-3} mol/l (Fig. 7), the difference in the order of addition of reagents slightly appears. Here, in the case of the addition in the order of Fe^{3+}, OH^-, SiO_3^{2-}, and HTAC, the optimum floatability of F=98% was obtained at the HTAC concentration of 2.0×10^{-3} mol/l, while in the case of the addition in the order of Fe^{3+}, SiO_3^{2-}, OH^-, and HTAC, the optimum floatability of F=94% was obtained at the HTAC concentration of 2.0×10^{-3} mol/l. The position of peaks are the same as that of Fig. 6, but the floatability is seen to decrease slightly with the increase of Fe^{3+} ions. On further increase of Fe^{3+} ions to 6.99×10^{-3} mol/l, the floatability showed a maximum of F=85.5% at the HTAC concentration of 1.4×10^{-3} mol/l for the addition in the order of Fe^{3+}, OH^-, SiO_3^{2-}, and HTAC, while a far smaller maximum of F=67.5% was obtained at the HTAC concentration of 2.61×10^{-3} mol/l for the addition in the order of Fe^{3+}, SiO_3^{2-}, OH^-, and HTAC.

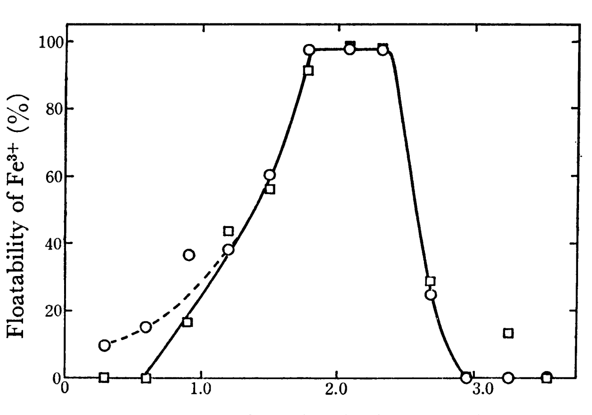


Fig. 6. Floatability *vs.* concn of HTAC for Fe^{3+}–SiO_3^{2-}–HTAC system. Fe^{3+}: 6.68×10^{-5} mol/l, SiO_3^{2-}: 1.58×10^{-2} mol/l, pH: 10.35.

—: Addition of Fe^{3+}, SiO_3^{2-}, OH^-, and HTAC in this order.

---: Addition of Fe^{3+}, OH^-, SiO_3^{2-}, and HTAC in this order.

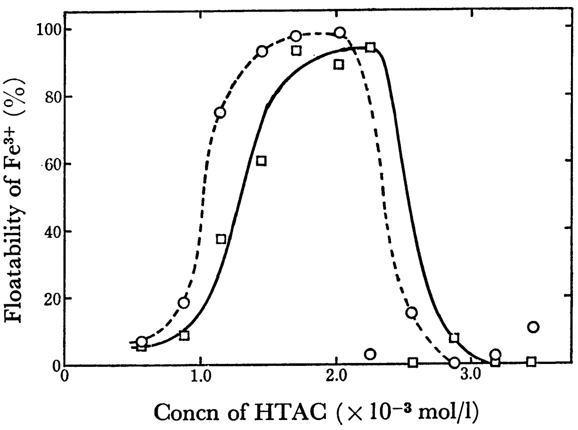


Fig. 7. Floatability *vs.* concn of HTAC for Fe^{3+}–SiO_3^{2-}–HTAC system. Fe^{3+}: 3.15×10^{-3} mol/l, SiO_3^{2-}: 1.56×10^{-2} mol/l, pH: 9.85.

—: Addition of Fe^{3+}, SiO_3^{2-}, OH^-, and HTAC in this order.

---: Addition of Fe^{3+}, OH^-, SiO_3^{2-}, and HTAC in this order.

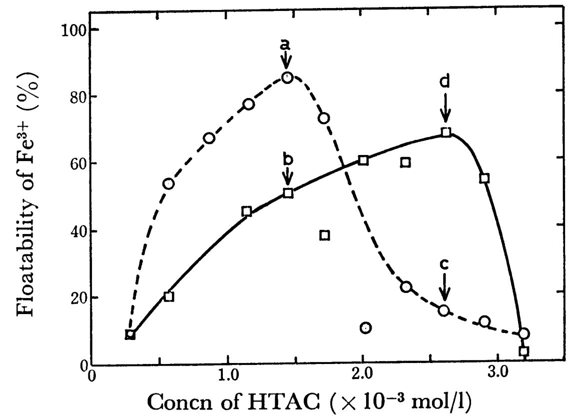


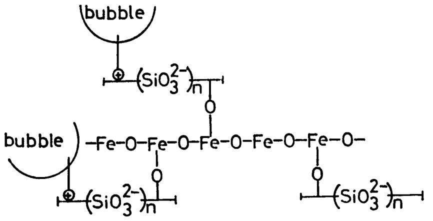
Fig. 8. Floatability *vs.* concn of HTAC for Fe^{3+}–SiO_3^{2-}–HTAC system. Fe^{3+}: 6.99×10^{-3} mol/l, SiO_3^{2-}: 1.56×10^{-2} mol/l, pH: 9.60.

—: Addition of Fe^{3+}, SiO_3^{2-}, OH,$^-$ and HTAC in this order.

---: Addition of Fe^{3+}, OH^-, SiO_3^{2-}, and HTAC in this order.

The above difference may be due to the difference in structure of the sublate formed. In order to investigate the compositions of the sublate at points *a*, *b*, *c*, and *d* in Fig. 8 and to elucidate the mechanism of flotation, the compositions of each sublate and the total precipitate were determined. These results are shown in Table 4. In the case of the addition in the order of Fe^{3+}, OH^-, SiO_3^{2-}, and HTAC, the polynuclear Fe^{3+} ions may form and combine with SiO_3^{2-}, resulting in coagulation and flotation. This may explain the effective flotation of Fe^{3+} with a smaller amount of cationic surfactant. On the other hand, each Fe^{3+} ion combines directly with a SiO_3^{2-} ion in the case of the addition in the order of Fe^{3+}, SiO_3^{2-}, OH^-, and HTAC. In this case, a larger amount of cationic surfactant is required at optimum floatability, as shown in Fig. 8. From these considerations together with the compositions given in Table 4, schematic structures of the sublate for the Fe^{3+}–SiO_3^{2-}–HTAC system have been presented in Fig. 9. As can be seen, in the case of system *a* the polynuclear Fe^{3+} ion forms, attaches to SiO_3^{2-}, and is effectively floated by HTAC, while in the case of system *b*, each Fe^{3+} ion combines rather directly with SiO_3^{2-} and is floated by HTAC, showing lower *F* values. In Fig. 9, the models are presented so that the numbers of moles of HTAC, Fe^{3+}, and SiO_3^{2-} in the precipitate are equal for the systems *a* and *b*. At higher concentrations of HTAC, it is evident from Fig. 9 that the increase of the composition of HTAC in the sublate *a* does not affect the wettability of the sublate (system *c*), while the increase of HTAC in the sublate *b* increases the floatability by the increase of the attachments of HTAC to the SiO_3^{2-}–Fe^{3+} complex having no HTAC (system *d*).

(a) $Fe^{3+}+OH^-+SiO_3^{2-}+HTAC$



(b) $Fe^{3+}+SiO_3^{2-}+OH^-+HTAC$

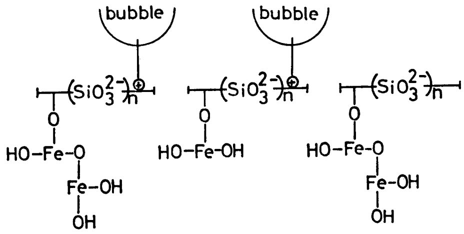


Fig. 9. Difference of sublate (precipitate) structure due to the difference of order of SiO_3^{2-} and HTAC addition.

TABLE 4. SUBLATE AND PRECIPITATE COMPOSITIONS AS AFFECTED BY THE ORDER OF SiO_3^{2-} AND HTAC ADDITION

No.	F (%)	Fe^{3+} (10^{-3} mol/l)[a)]	HTAC (10^{-3} mol/l)	SiO_3^{2-} (10^{-3} mol/l)
a	85.6	6.89(5.98)	1.48(1.48)	13.2(12.2)
b	50.6	6.93(3.54)	1.48(1.48)	13.9(11.6)
c	15.6	6.94(1.09)	2.60(2.60)	12.8(9.60)
d	67.5	6.92(4.72)	2.60(2.60)	13.7(12.0)

( ) Indicates sublate compositions.

a) The same as mentioned in Table 1.

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