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"Macromolecular Ion Flotation" of MnO_4^- by Combined Use of Macromolecular Anion and Cationic Surfactant

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MnO_4^- ions in aqueous solution were subjected to macromolecular ion flotation, a process of flotation applied for an aqueous solution containing organic or inorganic ions to be floated, macromolecular ions including macroscopic or colloidal particles with an ion exchange capacity and polymer ions, and oppositely charged ionic surfactant. The macromolecular anions examined were basic aluminum chloride, polyaluminum chloride, carboxymethylcellulose, sodium polyacrylate, sodium alginate, potassium poly(vinyl sulfate), sodium hexametaphosphate, polyphosphoric acid, polyacrylic acid, bentonite, and sodium metasilicate. As a cationic surfactant, hexadecyltrimethylammonium chloride was used. All the above substances are effective for the MnO_4^- ion flotation, whereas low molecular substances such as Na_3PO_4 are ineffective, when used with the cationic surfactant. Molecular models of sublate formed during the macromolecular ion flotation are proposed.

In our prevous papers,[1–2] we have confirmed that combined use of macromolecular or polymer anions, such as bentonite and silicate ions, with a cationic surfactant is effective for the flotation of both organic and inorganic anions and cations. The purpose of the present investigation is to examine whether or not macromolecular anions, including both macroscopic or colloidal particles with cation exchange capacity and polymer anions, are in general effective for ion flotation when used in combination with a cationic surfactant.

MnO_4^- ions were adopted as the ions to be subjected to flotation. The macromolecular ions tested were aluminum chloride ($AlCl_3$) and polyaluminum chloride ($PAlCl_3$) in basic solution, carboxymethylcellulose (CMC), sodium polyacrylate (NaPA), sodium alginate (NaAlg), potassium poly(vinyl sulfate) (KPVS), sodium hexametaphosphate (NaHMP), polyphosphoric acid (PPA), polyacrylic acid (PAA), bentonite (Bt), and sodium metasilicate (NaMS); NaHMP and PPA, not high molecules, were adopted since they behave similarly to high polymer ions with respect to the flotation. The cationic surfactant tested was hexadecyltrimethylammonium chloride (HTAC) which had shown good floatability for both anions and cations.

Experimental

Materials. Commercial products of pure grade were used for $AlCl_3$ ($AlCl_3 \cdot 6H_2O$), $PAlCl_3$ ($AlCl_3 \cdot nAl_2O_3$, Al_2O_3 content 30 wt%), CMC (dp, 700—850), NaPA (dp, 22000—66000), NaAlg (relative viscosity, 15.67 at 30 °C), KPVS (dp, 1500), NaHMP ($[NaPO_3]_6$), PPA ($P_6O_4H_{13}$), PAA (dp, 8000—12000), Bt (montmorillonite), NaMS ($Na_2SiO_3 \cdot 9H_2O$), trisodium phosphate (TNaP), and potassium permanganate.

Measurement. The concentration of silicate ions was measured colorimetrically at the wavelength 450 nm[3] from the color developed by adding an aqueous solution of ammonium molybdate to a sample liquor. The concentration of permanganate ions was determined by the usual titrimetric method using a solution of sodium oxalate. The concentration of each of the remainder was determined by dissolving its known amount of dried substance in water; concentration of $PAlCl_3$ could not be determined accurately due to its Al_2O_3 content indicated 30 wt%, being qualitative.

The solution to be subjected to flotation processing was prepared to contain MnO_4^- ions at a constant concentration around 1.6×10^{-4} mol dm^{-3}, proper amounts of one or some macromolecular ions and HTAC, a small amount of NaPA if necessay, and HCl or NaOH for pH control when needed. A volume (12 cm^3 for the systems of Table 1 and 10 cm^3 for the other systems) of the solution thus prepared was put into a stoppered test tube, 1.6 cm in inner diameter and 19 cm in ength, equipped with a stop cock at its bottom. It was slowly mixed and kept standing for 1 min, then vigorously shaken by hand to float MnO_4^- ions. After 5 min of standing, the lower portion was taken out and its MnO_4^- concentration was measured by use of a Shimazu Model Spectronic-20 spectrophotometer at wavelength 525 nm; the specific absorbance had been confirmed to be independent of the pH range 1—11 at this wavelength. The floatability of MnO_4^- ions was calculated from the difference between concentrations before and after the flotation processing on MnO_4^- ions.

Results and Discussion

Table 1 shows results of preliminary measurements on the MnO_4^- ion flotation by the combined use of macromolecular ions and HTAC. In these measurements, the concentration of MnO_4^- ions was kept constant at 1.59×10^{-4} mol dm^{-3} in average. The concentrations of macromolecular ions and HTAC are not necessarily for the optimum flotation condition; Table 1 is compiled

Table 1. Macromolecular ion flotation of MnO_4^-

Macromolecule Substance	Macromolecule Concn ppm	HTAC Concn ppm	NaPA Concn ppm	pH	Floatability/%
$AlCl_3$	996	55	1.67	9.8[a]	87
$PAlCl_3$	548	55	1.67	9.8[a]	88
CMC	666	833	—	6.3	100
NaPA	388	809	—	1.5[b]	98
NaAlg	1667	2447	—	6.8	98
KPVS	898	1691	—	1.1[b]	100
NaHMP	2196	3306	—	1.5[b]	100
PPA	10670	826	—	1.3	99
PAA	4514	1664	—	2.3	90
Bt	5839	662	—	8.8	100
NaMS	1314	500	—	11.2	98

a) NH_3 added. b) HCl added. $[MnO_4^-] = 1.59 \times 10^{-4}$ mol dm^{-3}. For the abbreviation of the substance names see text.

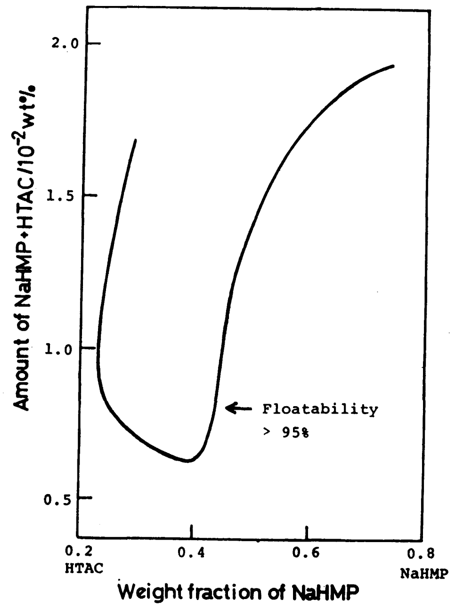

Fig. 1. Diagram of MnO_4^- ion flotation by NaHMP, HTAC, and HCl.
MnO_4^-: 1.49×10^{-4} mol dm^{-3}, pH: 1.4.

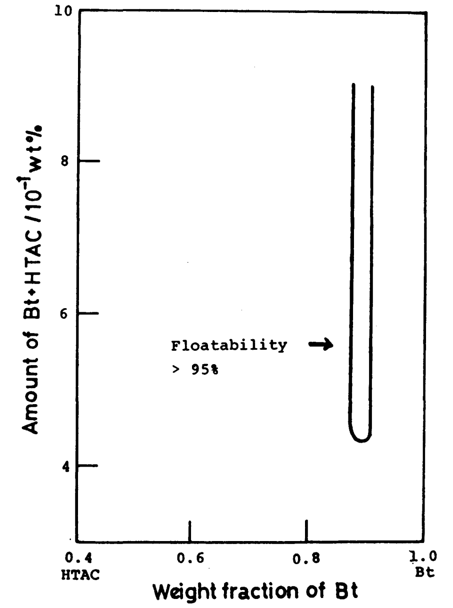

Fig. 2. Diagram of MnO_4^- ion flotation by Bt and HTAC.
MnO_4^-: 1.69×10^{-4} mol dm^{-3}, pH: 8.8.

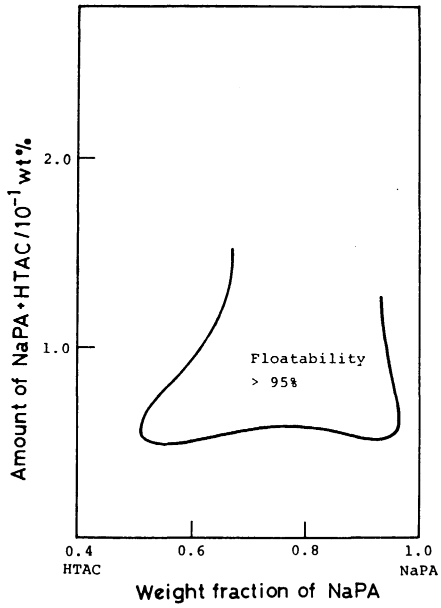

Fig. 3. Diagram of MnO_4^- ion flotation by NaPA, HTAC, and HCl.
MnO_4^-: 1.64×10^{-4} mol dm^{-3}, pH: 1.4.

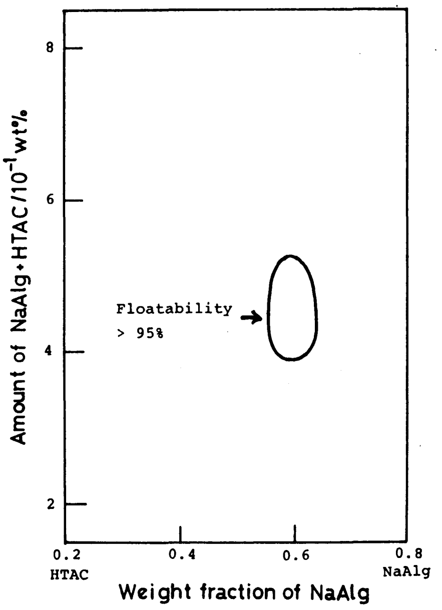

Fig. 4. Diagram of MnO_4^- ion flotation by NaAlg and HTAC.
MnO_4^-: 1.64×10^{-4} mol dm^{-3}, pH: 6.7.

merely to show a possibility of effective ion flotatition of MnO_4^- by combined use of macromolecular anions and cationic surfactant. As seen from Table 1, many macromolecular anions, when used with HTAC, are effective for the flotation of MnO_4^- ions, whereas low molecular electrolytes were found ineffective for that flotation, as exemplified by as low a floatability as 46% which TNaP showed at pH 1.1 (not indicated in Table 1). On the basis of this finding, the present authors propose the term "Macromolecular ion flotation" for such flotations as are effected by use of macromolecular or polymer ions and ionic surfactants both carrying charges opposite to each other; the present investigation has dealt with a case of combination of macromolecular anions with an cationic surfactant and the preceding paper[4] reported a case of effective use of poly(ethyleneimine) (cationic macromolecule) and sodium dodecyl sulfate (anionic surfactant).

For several systems in Table 1, flotation of MnO_4^- ions was studied in dedail by varying the ratio of macromolecular anions to HTAC and their total amount while the concentration of MnO_4^- ions was kept constant. The results obtained are shown in Figs. 1 to 5 for NaHMP+HTAC+HCl, Bt+HTAC, NaPA+HTAC+HCl, NaAlg+HTAC, and CMC+HTAC systems, respectively, each of which was treated similarly

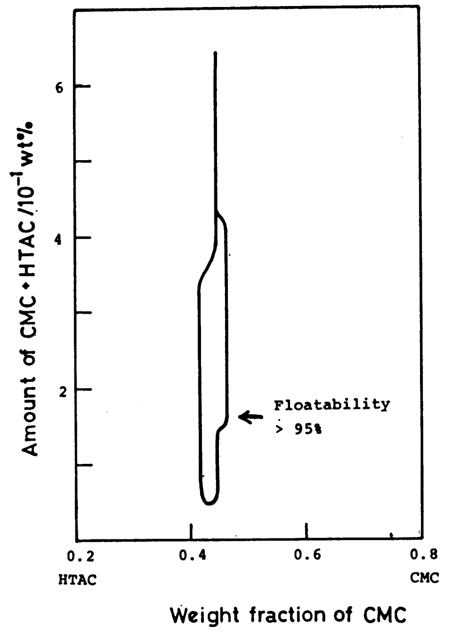

Fig. 5. Diagram of MnO_4^- ion flotation by CMC and HTAC.
MnO_4^-: 1.58×10^{-4} mol dm^{-3}, pH: 6.

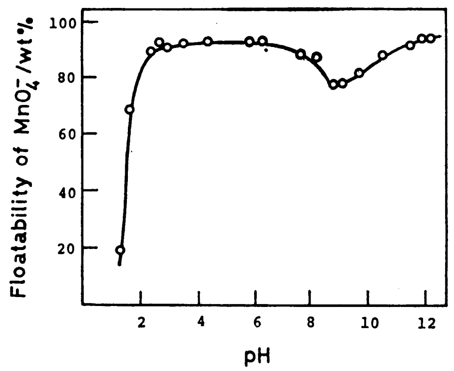

Fig. 6. Floatability of MnO_4^- ion *vs.* initial pH for NaMS+HTAC system.
MnO_4^-: 1.67×10^{-4} mol dm^{-3}, NaMS: 7570 ppm HTAC: 240.4 ppm.

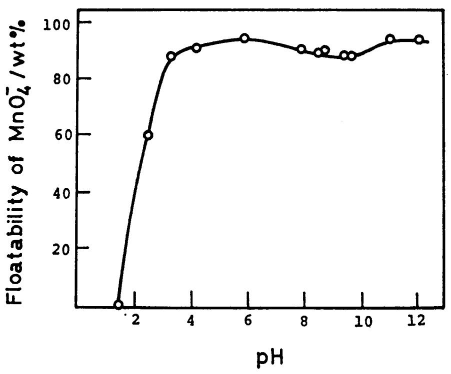

Fig. 7. Floatability of MnO_4^- ion *vs.* initial pH for NaAlg+HTAC system.
MnO_4^-: 1.67×10^{-4} mol dm^{-3}, NaAlg: 2000 ppm, HTAC: 2995 ppm.

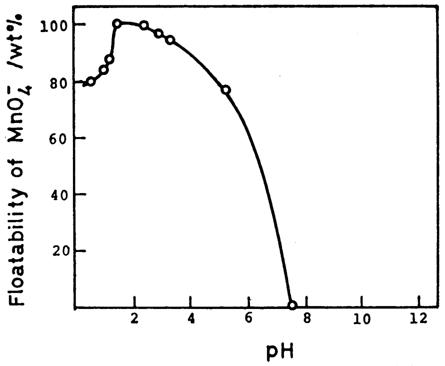

Fig. 8. Floatability of MnO_4^- ion *vs.* initial pH for NaPA+HTAC+HCL system.
MnO_4^-: 1.67×10^{-4} mol dm^{-3}, NaPA: 400.5 ppm, HTAC: 240.4 ppm.

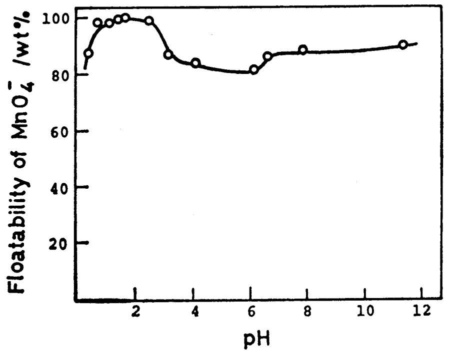

Fig. 9. Fostsbility of MnO_4^- ion *vs.* initial pH for NaHMP+HTAC system.
MnO_4^-: 1.67×10^{-4} mol dm^{-3}, NaHMP: 5365 ppm, HTAC: 5191 ppm.

to the NaMS+HTAC system already reported.[1] In each solution studied, the concentration of MnO_4^- ions and pH are given in the caption of each figure. In these diagrams, the floatability of the system is greater than 95% in the areas inside the curves. Thus we can confirm wide ranges of composition to be effective for ion flotation for the systems of Figs. 1 and 3, while we note narrow vertical ranges of the effective ion flotation, and only a small region for the system of Fig. 4. For the cases of Figs. 2 and 5, a nearly constant weight ratio of macromolecular ions to surfactant may be expected for the sublate composition, similarly to the case of NaMS+HTAC system already reported.[1]

To get the pH dependence of flotation efficiency of MnO_4^- ions, a study was made on the systems of NaMS+HTAC,** NaAlg+HTAC, NaPA+HTAC+HCl, and NaHMP+HTAC. The initial pH of solution was controlled by addition of HCl or NaOH. The results are shown in Figs. 6 to 9, where as a whole, floatabilities are seen to exceed 90% over a wide pH range, especially in acidic regions for the NaPA and NaHMP systems, attaining nearly 100%.

It is confirmed from the above results that the composition and total concentration of the set of macromolecular ions and surfactant as well as the pH of solution are important factors affecting the floatabiitly

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** The corresponding composition diagram has been shown in the preceding paper.[1]

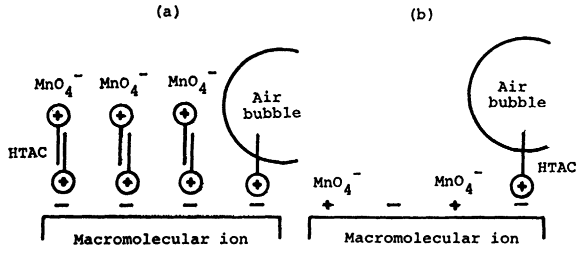

Fig. 10. Sublate structures of MnO_4^-+macromolecular ion+HTAC.
(a): The case of macromolecular anion, (b): the case of macromolecular ampholyte.

of MnO_4^- ions. In addition, it is noted that, although the NaPA+HTAC+HCl system is capable of effective MnO_4^- flotation in an acidic region, the system PAA with HTAC is not so effective at pH 2.3 as shown in Table 1. The reason is not clear at present, but it may be due to the different order of adding the flotation reagent, namely, in the former case, PAA is formed by the acidification after the reaction of NaPA with HTAC, while in the latter case, PAA is added without NaPA and this makes difficult the attachment of hexadecyltrimethylammonium ion to polyacrylate chain. These phenomena are similar to those observed in the case[1)] of MnO_4^- ion flotation by NaMS and HTAC where the order of adding NaMS and HTAC sensitively affects the floatability.

A probable model of MnO_4^- sublate is given in Fig. 10a, which has already been proposed in the case of macromolecular anions.[1)] On the other hand, for the case of ampholyte polymers like $AlCl_3$ and $PAlCl_3$ in alkaline solution, the model shown in Fig. 10b is applicable since it is in conformity with the observation, given in Table 1, that HTAC in less quantity than in the case of other macromolecular anions is capable of resulting in effective MnO_4^- flotation.

References

1) I. Takayanagi, K. Kobayashi, and T. Sasaki, *Bull. Chem. Soc. Jpn.*, **49**, 2419 (1976).

2) K. Kobayashi, K. Natori, M. Kamaya, and T. Sasaki, *Bull. Chem. Soc. Jpn.*, **51**, 439 (1978); T. Inakazu, K. Kobayashi, and T. Sasaki, *ibid.*, **48**, 3008 (1975); K. Kobayashi, H. Sato, K. Kachi, M. Nakamura, and T. Sasaki, *ibid.*, **48**, 3533 (1975); K. Kobayashi, N. Watabe, K. Hachisuka, and T. Sasaki, *ibid.*, **49**, 2701 (1976).

3) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd ed, Interscience Pub., New York (1956).

4) T. Sasaki, H. Kurosawa, K. Miyasaka, and M. Mizushima, *Bull. Chem. Soc. Jpn.*, **53**, 2506 (1980).