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Studies of the Ion Flotation by Poly(ethyleneimine) Resin

Tsunetaka SASAKI,* Hisayo KUROSAWA, Keiichi MIYASAKA,
and Minoru MIZUSHIMA
Department of Chemistry, Faculty of Science, Tokai University, 1117 Kitakaname, Hiratsuka 259-12

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Flotation of Crystal violet (CV^+), neucoccin (NC^-), CrO_4^{2-}, PO_4^{3-}, Fe^{3+}, and Cu^{2+} ions was studied with use of poly(ethyleneimine) resin (PEI) as an adsorbent, Na-polyacrylate or polyacrylamide as a coagulant and sodium dodecyl sulfate or hexadecyltrimethylammonium chloride as a frother. In line with the results of adsorption studies, NC^-, PO_4^{3-}, and CrO_4^{2-} ions were effectively floated from their dilute solutions but CV^+ was not floated so much. The most effective flotation was attained for CrO_4^{2-} ions, a rapid initial decrease in concentration due to the flotation within 30 s being followed by a gradual decrease and nearly 100% flotation achieved within 10 min for a dilute solution. The rate of flotation follows a bimolecular reaction. The activation energy of flotation, 28.03 kJ mol^{-1}, is equal to that of CrO_4^{2-} ion adsorption by PEI. Flotation of Fe^{3+} and Cu^{2+} ions was effectively carried out through chelate formation of these ions with PEI.

Adsorbing particle flotation has been reported as an effective method of ion flotation,$^{1)}$ bentonite being used as a cation exchange adsorbent. Further, poly(ethyleneimine) (PEI) was found to be a good anion exchange adsorbent as well as a chelating agent for metallic cations.$^{2)}$ The adsorbing particle flotation of organic and inorganic anions and cations using PEI is reported in this paper.

Experimental

Materials. PEI used was supplied by Shunan Petroleum Company. The sample was prepared in a similar way to that reported.$^{2)}$ Crystal Violet (CV^+) was precipitated by the addition of diethyl ether to an ethanol solution of CV^+. The precipitate was filtered and dried under reduced pressure. Neucoccin (NC^-) was recrystallized from its aqueous solution by the addition of anhydrous sodium carbonate. Crystals were filtered, washed with ethanol and dried. Potassium chromate, trisodium phosphate, Fe(III) chloride and Cu(II) sulfate of guaranteed grade were used without purification. Sodium polyacrylate (NaPA) of the degree of polymerization 2200—6600 and polyacrylamide (PAA) (Sanfloc AA-300P of Sanyo Chemical Industry Product) were used as coagulants. Pure hexadecyltrimethylammonium chloride (HTAC) (KAO Soap Co.) and sodium dodecyl sulfate (SDS) (Nikko Chemical Co.) were used.

Measurement. Flotation was carried out by adding PEI, coagulant and surfactant to the solution containing ions to be floated and shaking the solution in a stoppered test tube equipped with a stopcock at the bottom. Floatability (F) of dissolved ions was calculated from the concentrations of the solute before and after flotation by

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

where C_i and C_f denote the initial and final concentration of solute ions, respectively.

The concentrations of CV^+ and NC^- ions were measured with a Shimazu Spectronic Colorimeter 20 at wave lengths of 480 nm and 580 nm, respectively. The concentrations of CrO_4^{2-}, Fe^{3+}, and Cu^{2+} ions were measured with a Hitachi Atomic Absorption Spectrometer at wave lengths 357.9 nm, 248.3 nm, and 324.7 nm, respectively. Concentration of phosphate was determined by colorimetry at wave length 700 nm of ammonium phosphomolybdate formed by the addition of ammonium molybdate to the sample solution.

Results and Discussion

Flotation of PEI. In order to carry out the adsorbing particle flotation of ions by PEI, conditions for the flotation of PEI were studied. Flotation by hand-shaking of PEI suspension with addition of SDS alone, SDS and NaPA, and HTAC and NaPA was studied. In the flotation of PEI–SDS system, 15 cm^3 of a solution containing 0.1 g of PEI and varying amounts of SDS was shaken in a test tube for 10 s and left to stand for 5 min. The floatability was measured from the amount of PEI remaining as a suspension after flotation. In the flotation of PEI–NaPA–SDS and PEI–NaPA–HTAC systems, 15 cm^3 of the solution containing 0.1 g of PEI, 5.3 ppm of NaPA and varying amounts of SDS or HTAC was subjected to a similar treatment and the floatability was measured. All the experiments were carried out at room temperature, *ca.* 25 °C. The results are shown in Fig. 1.

The flotation percentage of PEI increases with increasing concentration of SDS or HTAC. The minimum concentration of surfactant of 100% flotation and the time required for the flotation are given in Table 1. Adsorbing particle flotation can be carried out under the conditions given. However, NaPA–SDS and NaPA–HTAC systems are preferable since flotation is quickly completed. NaPA–HTAC was used in the ion flotation studies of CV^+, NC^-, CrO_4^{2-}, and PO_4^{3-}, and PAA–SDS in the case of Fe^{3+} and Cu^{2+}

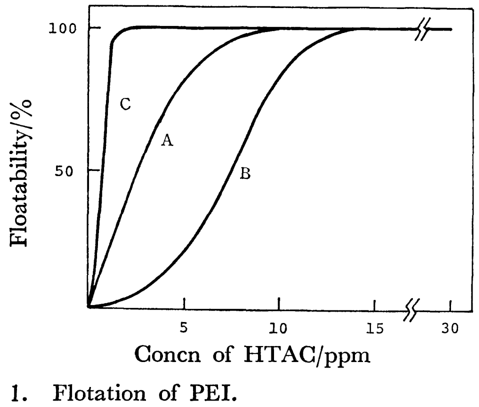

Fig. 1. Flotation of PEI.
A; SDS system, B; SDS-NaPA system,
C; HTAC-NaPA system.

Table 1. Flotation of PEI

System	Concn of SDS or HTAC	Time of flotation
SDS	8 ppm	60 s
SDS-NaPA	15	7
HTAC-NaPA	2	30

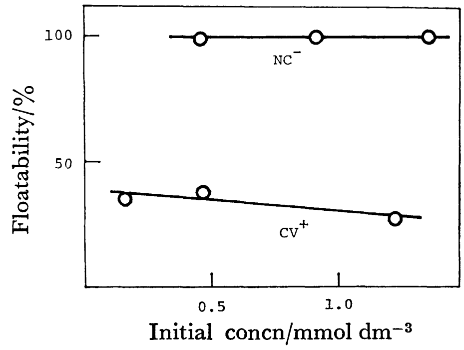

Fig. 2. Flotation of dyes.

ion flotation, neither NaPA–SDS nor NaPA–HTAC being effective in the latter case.

Flotation of Dye Ions. A 20 cm^3 solution containing 0.1 g of PEI, 14 ppm of NaPA in the case of NC$^-$, 40 ppm of NaPA in the case of CV$^+$, 20 ppm of HTAC and varying amounts of NC$^-$ or CV$^+$ ions was shaken frequently for 7 min. After complete float-up of PEI, concentrations of NC$^-$ and CV$^+$ ions in the underlying layers were measured, the floatability calculated being plotted against the initial concentration of respective ions (Fig. 2). Floatability of ions is nearly 100% up to the initial concentration of about 1.5 mmol dm^{-3}, while a maximum of 35% floatability was obtained for the dilute solution of CV$^+$ ions. Such a difference in floatability between NC$^-$ and CV$^+$ ions can be expected from the anion exchange nature of PEI.[2)]

Flotation of CrO_4^{2-} Ions. Since CrO_4^{2-} ions are significant as regards environmental contamination, removal of CrO_4^{2-} ions from aqueous solution by ion flotation was studied in detail.

Rate of CrO_4^{2-} Ion Flotation. A 150 cm^3 solution containing 1 g of PEI 13 ppm of NaPA, 3.3 ppm of HTAC and varying amounts of CrO_4^{2-} ions was put into an Erlenmeyer flask. Magnetic stirring for 5 min and shaking by hand was repeated. Residual concentration of Cr in the solution below PEI floated after each shaking was measured and plotted against time. Figure 3 shows the result for the solution of initial Cr concentration of 61.47 ppm.† The initial rapid fall of concentration within 30 s was followed by a gradual decrease, the concentration falling below 1/10 of the initial value within the first 10 min. Figure 4 shows the floatability of Cr after flotation for 10 min plotted against the initial concentration. The floatability increases with decreasing concentration of Cr, 98% of Cr being removed from 10.7 ppm Cr solution by flotation for 10 min.

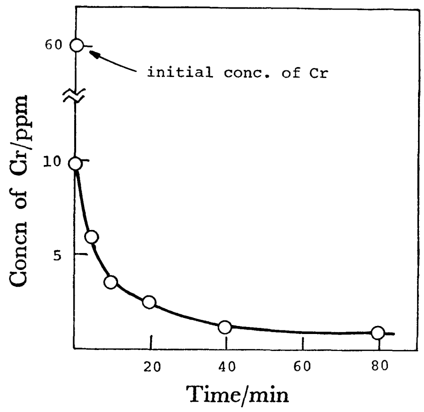

Fig. 3. Rate of CrO_4^{2-} ion flotation.

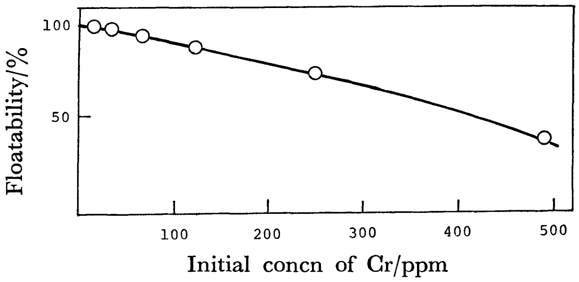

Fig. 4. Flotation of Cr.

In order to study the temperature dependence of the rate of CrO_4^{2-} ion flotation, a 500 cm^3 solution containing 54.5 ppm of Cr, 1 g of PEI, 14 ppm of NaPA and 4 ppm of HTAC was put into the Erlenmeyer flask. Stirring and shaking were carried out as mentioned above. The residual concentration determined after each flotation by shaking was measured, the result being plotted against time at a constant temperature in the range 25 °C—50 °C. Diagrams similar to that in Fig. 3 were obtained. From the results $1/(C-C_\infty)$ *vs.* t plots were made as in the case of CrO_4^{2-} ion adsorption by PEI,[2)] where C and C_∞ denote the concentrations of Cr at time t and after a sufficiently long time, respectively. The results obtained at 30 °C are shown in Fig. 5. A linear relation

$$\frac{1}{C-C_\infty} = Kt + L$$

where K and L are constants, was confirmed to hold. This indicates that the reaction is bimolecular as in the case of CrO_4^{2-} ion adsorption by PEI.[2)] The logarithm of K, considered as a reaction rate constant

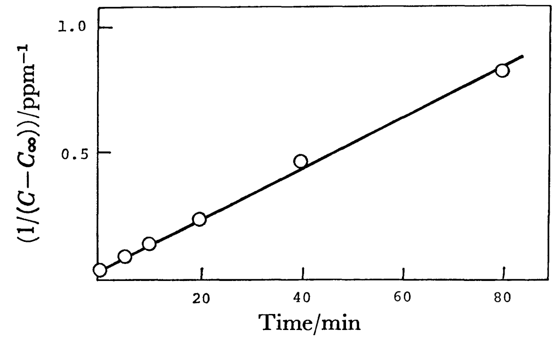

Fig. 5. $(1/C-C_\infty)$ *vs.* t plots.

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† Concentration of Cr and the following P are expressed by ppm instead of mol dm^{-3}.

of ion flotation, is plotted against the reciprocal of the absolute temperature T (Fig. 6). A straight line was obtained, the slope of which gave the activation energy of 28.03 kJ mol^{-1} in agreement with the value obtained for CrO_4^{2-} ion adsorption by PEI.[2] This suggests that the ion exchange adsorption is the rate determining step of the flotation of CrO_4^{2-}.

Effect of the Amount of PEI on CrO_4^{2-} Ion Flotation. In order to determine the amount of PEI necessary for CrO_4^{2-} ion flotation, a 500 cm^3 solution containing 5 ppm of Cr,[††] 14 ppm of NaPA, 4 ppm of HTAC and varying amounts of PEI was stirred and shaken in an Erlenmeyer flask, and the residual concentration of Cr after flotation for 10 min was measured. The result is plotted against the amount of PEI in Fig. 7. It was confirmed that 0.5 g of PEI is sufficient to reduce Cr concentration from 5 ppm to below 0.5 ppm in a 500 cm^3 solution. Since neither the NaPA–HTAC–CrO_4^{2-} system nor the HTAC–CrO_4^{2-} system showed any perceptible flotation of Cr, PEI together with HTAC and NaPA is considered necessary to float Cr. A suggested model to explain the mechanism of adsorbing particle flotation of CrO_4^{2-} ions is shown in Fig. 8.

Flotation of PO_4^{3-} Ions. A 500 cm^3 solution containing 1 g of PEI, 14 ppm of NaPA, 8 ppm of HTAC and varying amount of PO_4^{3-} was treated as in the case of CrO_4^{2-} ion flotation. The residual concentration of P, determined by the measurement of PO_4^{3-} ion concentration, was plotted against the flotation time. Figure 9 shows results obtained for PO_4^{3-} solution containing 8.15 ppm of P. An abrupt decrease in the residual concentration of P within a minute is followed by a gradual decrease, the concentration becoming nearly constant after 20 min flotation. Figure 10 shows the floatability of P after 20 min flotation plotted against the initial concentration. The floatability does not reach 90% even in a dilute solution of PO_4^{3-} ions. Further experiment showed that 1 g of PEI is necessary to reduce the concentration of P from 3.26 ppm to 0.23 ppm in 500 cm^3 solution by 40 min flotation.

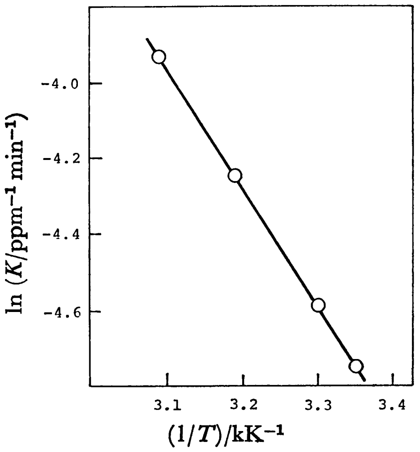

Fig. 6. Arrhenius plots.

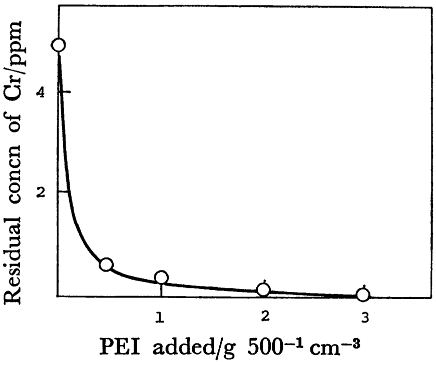

Fig. 7. Removal of Cr by flotation.

Rate of Fe^{3+} and Cu^{2+} Ion Flotation. While the use of NaPA and HTAC was found to be unfavorable, that of PAA and SDS was effective. Preliminary experiments showed 57 ppm of SDS and 10 ppm of

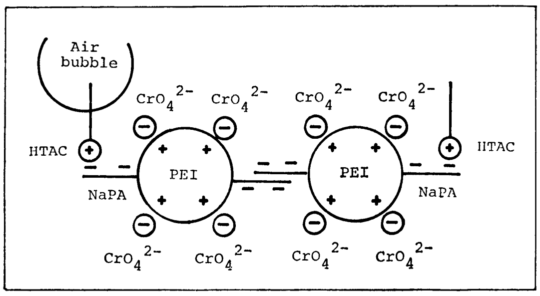

Fig. 8. Model of CrO_4^{2-} ion flotation by PEI, NaPA, and HTAC.

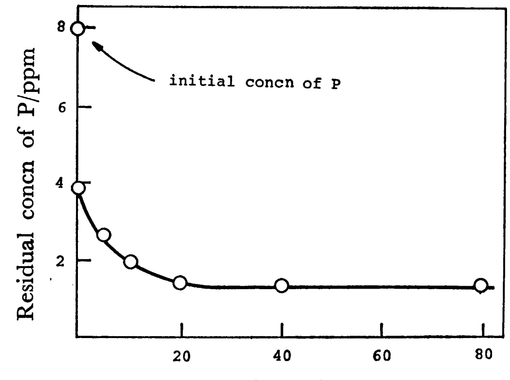

Fig. 9. Rate of flotation of P.

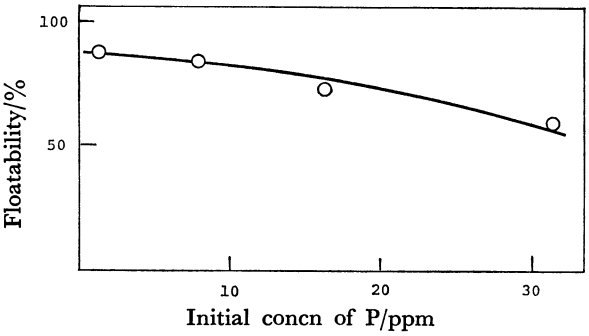

Fig. 10. Concentration *vs.* floatability of P.

[††] Ten times the maximum permissible concentration of Cr in environmental water.

PAA to be necessary.

For the measurement, a 20 cm^3 solution containing 1×10^{-4} mol dm^{-3} of Fe^{3+} ions at pH 8 or Cu^{2+} ions at pH 7, 0.06 g of PEI, 57 ppm of SDS and 10 ppm of PAA was gently shaken in a test tube for varying periods of time and then shaken vigorously for 3 s. PEI underwent flotation. The concentrations of Fe^{3+} and Cu^{2+} ions in the underlying layers after shaking were determined, floatability calculated being plotted against time. It was found that the maximum floatability reaches nearly 100% and 90% after 30 s of flotation for Fe^{3+} and Cu^{2+} ions, respectively.

Effect of pH *on Fe*$^{3+}$ *and Cu*$^{2+}$ *Ion Flotation.* The pH of a 20 cm^3 solution containing 1×10^{-4} mol dm^{-3} of Fe^{3+} or Cu^{2+} ions, 57 ppm of SDS, 10 ppm of PAA and 0.06 g of PEI was controlled by the addition of HCl and NaOH. The solution was gently shaken for 30 s, then vigorously for 3 s and PEI was floated. Fe^{3+} and Cu^{2+} ion concentrations were measured and the floatability calculated. The floatability is plotted against pH in Fig. 11. Flat maximum of floatability is attained in the pH range 5—9 for Fe^{3+} and 4—9 for Cu^{2+} ions. The pH dependence of floatability of Fe^{3+} and Cu^{2+} ions without the addition of PEI is also given for the sake of comparison. The floatability is far smaller than that of the system with PEI, showing the marked effect of PEI for the flotation of these ions.

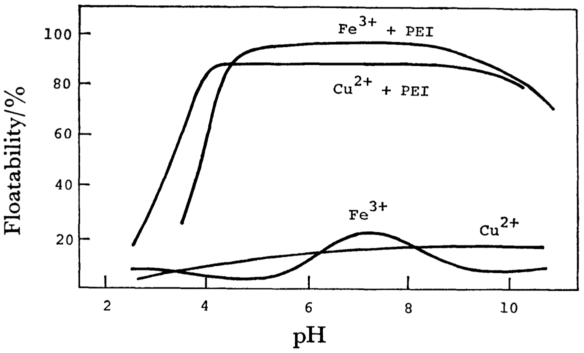

Fig. 11. pH *vs.* floatabilities of Fe^{3+} and Cu^{2+}.

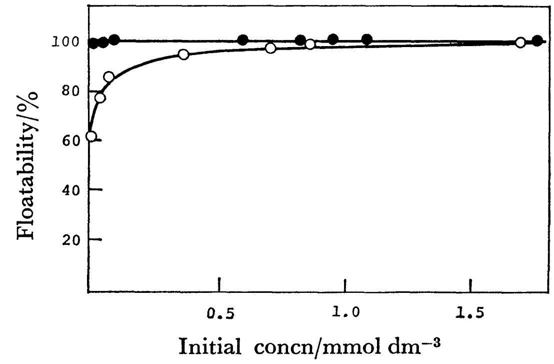

Fig. 12. Flotation of Fe^{3+} (●) and Cu^{2+} (○) ions.

Concentration Dependence of Fe^{3+} *and Cu*$^{2+}$ *Ion Flotation.* A 20 cm^3 solution containing 57 ppm of SDS, 10 ppm of PAA, 0.06 g of PEI and varying amounts of Fe^{3+} ions at pH 8 or Cu^{2+} ions at pH 7 was gently shaken for 30 s, then vigorously for 3 s and PEI was floated. Fe^{3+} and Cu^{2+} ion concentrations of underlying layer were measured, the floatability calculated being plotted against the initial concentration of these ions (Fig. 12). Nearly 100% flotation was observed in wide concentration ranges of these ions, except for a lower concentration of Cu^{2+} ions where a decrease in floatability was observed. The decrease may be due to the hydrolytic formation of hydroxide which is neither adsorbed by PEI nor floated without PEI.

References

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