The Flotation of Cd^{2+} Ions in the Presence and Absence of Zn^{2+} Ions

Koichi Kobayashi,*,† Yoshiko Shimizu,†† and Tsunetaka Sasaki†††

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo 158

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The flotation of Cd^{2+} ions was investigated in the presence and absence of Zn^{2+} ions. It was found that the flotation efficiency of Cd^{2+} ions in the Cd^{2+}–anionic surfactant system is markedly small in the presence of Zn^{2+} ions, but the flotation efficiency of Cd^{2+} ions in the Cd^{2+}–bentonite–cationic surfactant system (adsorbing particle flotation) decreased only slightly in the presence of Zn^{2+} ions. The flotation efficiency in the latter case was further increased by the addition of 3 ppm of polyacrylamide. The doubling of the flotation reagents and time did not effectively increased the flotation efficiency of Cd^{2+} ions in the presence of Zn^{2+} ions, but the two-stage flotation did. It was confirmed that the adsorbing particle flotation of Cd^{2+} ions would be an excellent method in the presence of Zn^{2+} ions.

In previous papers,[1,2] we reported that Cd^{2+} ions were effectively removed by using an anionic surfactant, a cationic surfactant with bentonite, or a cationic surfactant with bentonite and polyacrylamide.

Generally, mine water contains such heavy metal ions as Cd^{2+}, Cu^{2+}, and Zn^{2+}. In the case of removal of Cd^{2+} ions, the flotation is greatly influenced by co-existing ions.

Shimoiizaka *et al.*[3] have studied the removal of Cd^{2+} ions by precipitation flotation in the presence of co-existing ions, such as Fe^{2+} and Zn^{2+} ions, and have indicated that Cd^{2+} ions could be effectively removed by xanthate in the presence of these co-existing ions. However, no other studies have been reported on the adsorbing particle flotation of Cd^{2+} ions in the presence of co-existing ions.

In the present paper, the flotation of Cd^{2+} ions in the presence and absence of Zn^{2+} ions will be reported.

Experimental

Materials. The zinc(II) nitrate used was of an extra-pure grade $Zn(NO_3)_2 \cdot 6H_2O$; it was recrystallized twice from distilled water, and a stock solution with a concentration of 1.78×10^{-3} mol/dm³ was prepared. For the determination of the concentration of Zn^{2+}, the chelate-titration method was carried out using Cu-PAN.[4] A stock solution of Cd^{2+} ions was prepared by dissolving Cd metal of a 99.999% purity in nitric acid. All the other reagents, such as disodium α-sulfonatododecanoate (α-SLNa), dodecyltrimethylammonium chloride (DTAC), and bentonite (Bt), were the same as have been described previously.[1] The polyacrylamide (PAA) used as a coagulating agent was a product of the Mitsubishi Kasei Co., Ltd., its average molecular weight was seven million.

Apparatus and Procedure. The apparatus and the method of flotation measurements were the same as have been reported previously.[1] The concentration of the Cd^{2+} ions was measured by using an atomic absorption spectrometer (Techtron Pty., Model-AA-100). A glass electrode pH meter (Toadenpa Co., Ltd., HM-5A) was used to measure the pH. The gas-flow rate was kept at 10 ml/min, while the gas-flow time was kept at 7 or 14 min, as the case required. The measurements of the flotation were carried out at a room temperature of about 25 °C.

The flotation efficiency of Cd^{2+} ions (F) is conventionally expressed by:

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

where C_i and C_f are the initial and final concentrations of the Cd^{2+} ions respectively.

Results and Discussion

The adsorbing particle flotation was carried out for a solution containing 1.78×10^{-5} mol/dm³ Cd^{2+}, 1.78×10^{-5} mol/dm³ DTAC, or 1.78×10^{-4} mol/dm³ DTAC and 100 ppm Bt. The results are shown in Fig. 1. As can be seen in Fig. 1, the flotation efficiency of the Cd^{2+} ions increased with an increase in the pH, showed a maximum at about pH 11, and decreased with an increase in the pH above about pH 11. The maximum flotation efficiencies of the Cd^{2+} ions were 73% and 96% in the cases of 1.78×10^{-5} mol/dm³ DTAC and 1.78×10^{-4} mol/dm³ DTAC respectively. In the former case, the Cd^{2+} ions may be completely adsorbed on the Bt particle, considering the results presented in a previous paper,[2] but the Bt particle

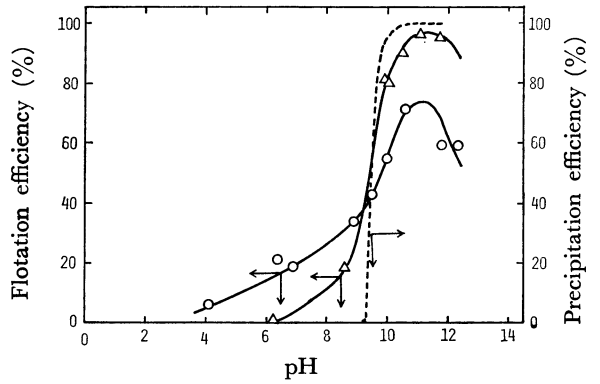

Fig. 1. Flotation efficiency *vs.* pH for Cd^{2+}–Bt–DTAC system. Cd^{2+}: 1.78×10^{-5} mol/dm³, Bt: 100 ppm, DTAC (○: 1.78×10^{-5} mol/dm³; △: 1.78×10^{-4} mol/dm³), gas-flow time: 7 min, gas-flow rate: 10 ml/min. ----: Precipitation efficiency *vs.* pH curve.

† Present address: Laboratory of Chemistry, Musashi Institute of Technolgy, 1-28-1, Tamatsutsumi, Setagaya, Tokyo 158.

†† Present address: 2-7-6, Shiomidai, Isogo-ku, Yokohama, Kanagawa 247.

††† Present address: Department of Chemistry, Faculty of Science, Tokai University, Hiratsuka, Kanagawa 259-12.

could not be floated because the amount of DTAC was insufficient. When the concentration of DTAC increased to 1.78×10^{-4} mol/dm^3 DTAC, a nearly complete flotation of Bt particle could be attained. The broken curve in Fig. 1 represents the precipitation efficiency *vs.* pH curve obtained from the solubility product (7.6×10^{-15}) of $Cd(OH)_2$. It was confirmed that the flotation efficiency *vs.* pH curve of Cd^{2+} ions was in accord with the precipitation efficiency *vs.* pH curve of $Cd(OH)_2$. Judging from these facts, the polynuclear cations of Cd^{2+} may be formed and subsequently adsorbed on Bt particles. The Bt particles coagulated by DTAC are floated by bubbles.

The flotation of the Cd^{2+} ions was further carried out for the system prepared by adding 1.78×10^{-4} mol/dm^3 Zn^{2+} to a solution containing 1.78×10^{-5} mol/dm^3 Cd^{2+}, 1.78×10^{-5} mol/dm^3 DTAC, and 100 ppm Bt. The results are shown in Fig. 2(I). The flotation efficiency of the Cd^{2+} ions decreased to 62% when ten times as many Zn^{2+} ions were added as compared with 73% for the system without Zn^{2+} ions (Fig. 1). The decrease in the flotation efficiency of the Cd^{2+} ions may be due to Cd^{2+} being hindered by the adsorption of Zn^{2+} on the Bt surface. The flotation efficiency *vs.* pH curve of the system with Zn^{2+} ions shifts toward a lower pH as compared with that of the system without Zn^{2+} ions (Fig. 1). This shift in pH may be caused by the coprecipitation of Cd^{2+} with $Zn(OH)_2$, which was formed at about pH 7.7.

Figure 2(II) shows the results of the flotation of Cd^{2+} ions from a solution containing 1.78×10^{-5} mol/dm^3 Cd^{2+}, 1.78×10^{-5} mol/dm^3 α-SLNa, and 1.78×10^{-4} mol/dm^3 Zn^{2+}. The maximum flotation efficiency of 38% was obtained at pH 8.3. As may be seen, the flotation efficiency of the Cd^{2+}–α-SLNa system was lower than that of the Cd^{2+}–Bt–DTAC system in the presence of Zn^{2+} ions.

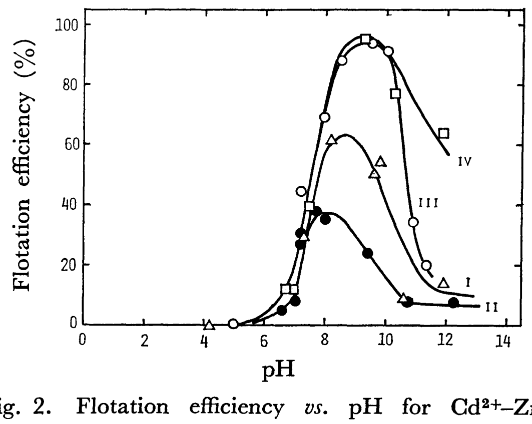

Fig. 2. Flotation efficiency *vs.* pH for Cd^{2+}–Zn^{2+}–Bt–DTAC system(I), Cd^{2+}–Zn^{2+}–α-SLNa system(II), Cd^{2+}–Zn^{2+}–Bt–DTAC–PAA system(III), and Cd^{2+}–Zn^{2+}–Bt–DTAC–PAA system(IV). Cd^{2+}: 1.78×10^{-5} mol/dm^3, Zn^{2+}: 1.78×10^{-4} mol/dm^3, gas-flow rate: 10 ml/min.
(I) DTAC: 1.78×10^{-5} mol/dm^3, Bt: 100 ppm, gas-flow time: 7 min. (II) α-SLNa: 1.78×10^{-5} mol/dm^3, gas-flow time: 7 min. (III) DTAC: 1.78×10^{-5} mol/dm^3, Bt: 100 ppm, PAA: 3 ppm, gas-flow time: 7 min. (IV) DTAC: 3.56×10^{-5} mol/dm^3, Bt: 200 ppm, PAA: 6 ppm, gas-flow time: 7 min.

In order to study the effect of PAA on the flotation efficiency, the flotation was carried out for a system prepared by adding 3 ppm PAA to a solution containing 1.78×10^{-5} mol/dm^3 Cd^{2+}, 1.78×10^{-4} mol/dm^3 Zn^{2+}, 1.78×10^{-5} mol/dm^3 DTAC, and 100 ppm Bt. As compared with Fig. 2(I) for the system without PAA, a sharp maximum of 95% flotation at about pH 9.5 is shown in Fig. 2(III). Thus, it was confirmed that the flotation efficiency of the Cd^{2+} ions increased further upon the addition of PAA.

The adsorbing particle flotation was further carried out by doubling the amount of reagents and the gas-flow time for the above system. However, the flotation efficiency of Cd^{2+} ions was not increased significantly. As can also be seen from Fig. 1 and other data,[1] the 1.78×10^{-4} mol/dm^3 DTAC is required to increase effectively the removal of 100 ppm Bt. Therefore, the further addition of DTAC is considered to increase the flotation efficiency of Cd^{2+} ions in the case of Fig. 2(IV).

As can also be seen from Fig. 1 and Fig. 2(I), the influence of the Zn^{2+} addition to the Cd^{2+}–Bt–cationic surfactant system is small in terms of the flotation efficiency. In the case of the presence of Zn^{2+}, the flotation efficiency of the Cd^{2+} ions of the Cd^{2+}–α-SLNa system was lower than that of the Cd^{2+}–Bt–DTAC system, as is shown by Fig. 2(I) and Fig. 2(II). These facts show that the adsorbing particle flotation is an effective method in the presence of Zn^{2+} ions. Further, the addition of 3 ppm PAA to the Cd^{2+}–Bt–DTAC system markedly increases the flotation efficiency of the Cd^{2+} ions, as may be seen by comparing the systems of Fig. 2(I) and Fig. 2(III). As can be seen in Fig. 2(IV), the maximum flotation efficiency of 96% was obtained when the concentration of each reagent was twice that of Fig. 2(III). Therefore, the flotation efficiency of the Cd^{2+} ions is not significantly increased by doubling the amount of the reagents and the gas-flow time.

It has also been known that the two-stage flotation is effective for the ion flotation.[5,6] Therefore, the flotation of Cd^{2+} ions from a solution containing 1.78×10^{-5} mol/dm^3 Cd^{2+}, 1.78×10^{-5} mol/dm^3 DTAC, 1.78×10^{-4} mol/dm^3 Zn^{2+}, 100 ppm Bt, and 3 ppm PAA was carried out at pH 9.55 in two stages. The flotation efficiency of Cd^{2+} ions in the first stage was 92.5%. After the underlying solution had been removed from the flotation cell, the second-stage flotation of the solution was carried out with the further addition of 1.78×10^{-5} mol/dm^3 DTAC, 100 ppm Bt, and 3 ppm PAA. It is evident from Table 1 that the flotation efficiency of the Cd^{2+} ions was 99%. From these facts, the removal of the Cd^{2+} ions can be said to have been almost complete after the two-stage flota-

Table 1. Flotation efficiency in two stages

pH	F (%)		Relative time and amount of reagents
	1st	1st+2nd	
9.55	92.5	99.0	2

tion.

In conclusion, the Cd^{2+} ions were effectively removed by using Bt and DTAC rather than the α-SLNa, and the flotation efficiency was further increased by the addition of PAA to the former system in the presence of Zn^{2+} ions. A two-stage flotation was found to be most effective.

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