Studies on the Separation of Cadmium from Solutions by Foam Separation. I. Foam Separation of Cadmium Cations

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Abstract

The efficiency of Cd^{2+} foam separation with sodium lauryl sulfate and sodium laurate from sodium sulfate and sodium nitrate solution was tested. Foam fractionation of Cd^{2+} with lauryl sulfate in the form of a hydrated ion pair $2C_{12}H_{25}SO_{4}^{-}, Cd^{2+}$ is ineffective because of a low recovery and high hydration of the foam. But ion flotation of Cd^{2+} as a low-solubility salt $(C_{12}H_{25}COO)_2Cd$ is highly effective. The presence of electrolyte in the solution has a negative influence on Cd^{2+} foam fractionation with lauryl sulfate because of an increase of inert salt concentration which causes competition for the collector between colligend Cd^{2+} and the added Na^+ ions, and because of simultaneous increase in the thickness of water sheaths around the gas bubbles. In the case of ion flotation with sodium laurate, the presence of electrolyte improves Cd^{2+} recovery and decreases the thickness of the water sheaths around the gas bubbles. The interpretation of the results is based on the exchange of the collector counterions as well as on the properties of the reaction products.

INTRODUCTION

Many industrial wastewaters contain cadmium in high concentrations because of the production of pigments and plating. One of several reasons for excluding this element is because of its toxicity. One of the methods frequently used for cadmium separation from solutions is precipitation of its hydroxide or sulfide. There is an urgent need for the development of new methods in chemical technology which would eliminate filtration of the sediment and which could be used for large volumes of extremely dilute

solutions. This problem led the author to take up basic studies involving foam separation of cadmium ions. Foam separation of cadmium has been studied recently by several investigators. Ferguson et al. (*1*) reported their attempts at cadmium removal by precipitate flotation of CdS and by adsorbing colloid flotation with FeS, using hexadecyltrimethylammonium bromide as a collector. The removal of cadmium in the presence of a high concentration of certain other metallic ions (such as Ca, Mg, Na, Hg, Cu, and Ni) by ion flotation with a chelating surfactant (i.e., 4-dodecyldiethylenetriamine) was reported by Okamoto and Chau (*2–5*). Huang and Wilson (*6*) studied precipitate flotation of CdS and $Cd(OH)_2$, and adsorbing colloid flotation of Cd with $Al(OH)_3$, $Fe(OH)_3$, and CuS. Sodium lauryl sulfate and hexadecyltrimethylammonium bromide were used as collectors. Kubota et al. (*7*) presented a great deal of data on Cd foam separation with an anionic surfactant. Kobayashi et al. (*8–10*) reported that Cd was effectively removed by ion flotation and precipitate flotation with an anionic surfactant by adsorbing colloid flotation using bentonite and polyacrylamide as coagulating agents. Shimoiizaka et al. (*11*) studied Cd removal by precipitate flotation with xanthate. Skrylev et al. (*12, 13*) reported the removal of Cd, Zn, Ni, and Pb by ion flotation and precipitate flotation using potassium laurate as the collector. Walkowiak and Grieves (*14*), by taking into account the differences in the stabilities of Zn, Cd, Hg, and Au cyanide complexes, determined the selective flotation conditions of these metals with NaCN and the cationic surfactant hexadecyltrimethylammonium chloride. In addition, Walkowiak et al. (*15*) reported selective foam separation of Zn, Cd, Hg, and Au chloride anion complexes from acidic aqueous solutions with a cationic surfactant.

In this article new information characterizing the process of cadmium separation (such as gas bubble hydration and the solubility of collector–metal ion compounds in the presence of inert electrolytes) has been obtained. The results are presented in three parts: foam separation of cations, precipitate flotation of hydroxide, and ion flotation of complex anions.

EXPERIMENTAL

Foam separation was conducted from solutions containing 10^{-4} M/dm^3 Cd^{2+} in double-distilled water at pH 6.4. As collectors, sodium lauryl sulfate (BDH Laboratory Division, England), sodium laurate (Ferak, Berlin, GDR), and sodium stearate (Carlo Erba, Milan) were used. All other reagents were made by POCH Gliwice (Poland), and they were of analytical purity grade. The collectors were dissolved in the solution of

Cd^{2+} in stoichiometric amounts. As these substances were used in methanol solutions, the flotation solutions contained 2% of methanol.

Flotation was conducted according to the method commonly used in a glass multibubble column, 26 cm high, 200 cm^3 in volume, and with a G-3 sinter at the bottom. The flotation process was conducted for 10 min at a constant flow rate of N_2 equal to 50 cm^3/min.

Single-bubble flotation and measurements of gas-bubble hydration were carried out by means of an apparatus described earlier (*16*).

The effectiveness of foam separation was estimated from determinations of Cd^{2+} or lauryl sulfate concentration in the initial and residual bulk flotation solutions. The determinations of Cd^{2+} were done polarographically using a polarograph (LP Laboratorni Pristrije, Prague) to the nearest 3%. As basic electrolyte, 1 N KCl with the addition of Na_2SO_3 was used in order to eliminate the oxygen wave (*17*). Because sulfite ions produce their own wave in a strongly acidic medium, the solutions were neutralized by anhydrous Na_2CO_3 prior to determinations. The residual-flotation suspension which contains low-solubility cadmium soaps was decomposed by boiling with HNO_3 before Cd^{2+} determination, and then neutralized with Na_2CO_3. The concentration of lauryl sulfate was determined by the colorimetric method with methylene blue (*18*).

Electric surface potential was measured using the ionization method which can be found in the literature (*19, 20*). The ionization method with ^{239}Pu as the source of α-particles was applied. The activity of the source was 10 mCi. The potential value was measured in the following systems: calomel electrode/Cd^{2+} solution or Cd^{2+}, SO_4^{2-}, and lauryl sulfate solution–air/Au. ΔV is the difference between the value of the surface potential of the basic $CdSO_4$ solution at 10^{-4} M/dm^3 concentration and the surface potential of the flotation solution which contains lauryl sulfate and sodium sulfate.

RESULTS

In the process of foam separation of Cd^{2+}, sodium lauryl sulfate and sodium soaps (laurate and stearate) were used as collectors. The removal of Cd^{2+} was studied in relation to the concentration of sodium nitrate and sulfate and also to that of the collector. The results of these studies are presented in Fig. 1, 2, and 5. It appears from Fig. 1 that, together with the increase in the concentration of the electrolyte in the solution up to 0.3 M/dm^3, the removal of Cd^{2+} by means of lauryl sulfate decreases distinctly from about 40 to 10% and is lower in sulfate than in nitrate solutions. In contrast, the removal of lauryl sulfate increases from ~30 to 80% as the electrolyte concentration increases and is higher in sulfate than in nitrate
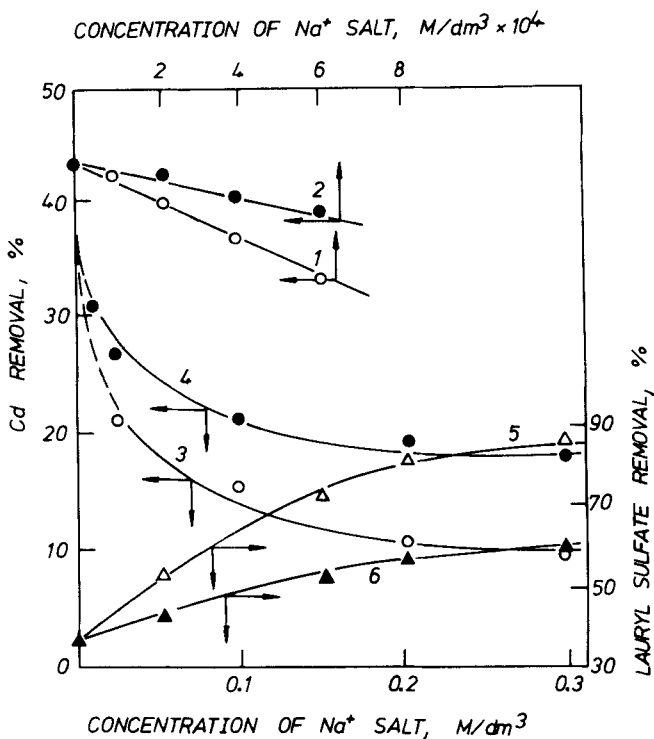
CONCENTRATION OF Na⁺ SALT, M/dm³ × 10⁴

FIG. 1. Effect of electrolyte concentration (1, 3, 5—Na_2SO_4 and 2, 4, 6—$NaNO_3$) on removal of Cd^{2+} (1–4) or lauryl sulfate (5, 6).

solutions. Thus a negative influence of the salt on the metal cation foam fractionation is observed, and at the same time a positive influence on foaming of lauryl sulfate occurs. In this series of experiments the collector was used in stoichiometric amounts for Cd^{2+} concentration, i.e., 2×10^{-4} M/dm^3.

In Fig. 2 the effect of alkyl sulfate concentration on cadmium removal is illustrated. This figure shows that with an increase in alkyl sulfate concentration up to 3×10^{-4} M/dm^3, the removal increases and then remains practically constant. However, higher removal was obtained from solutions at smaller sodium sulfate concentrations. In this case the increase in removal was caused by larger and larger amounts of the collector molecules added, for they are capable of binding Cd^{2+} ions.

From visual observation it was seen that the combination of alkyl sulfate with Cd^{2+} is completely soluble; furthermore, the foam transporting the
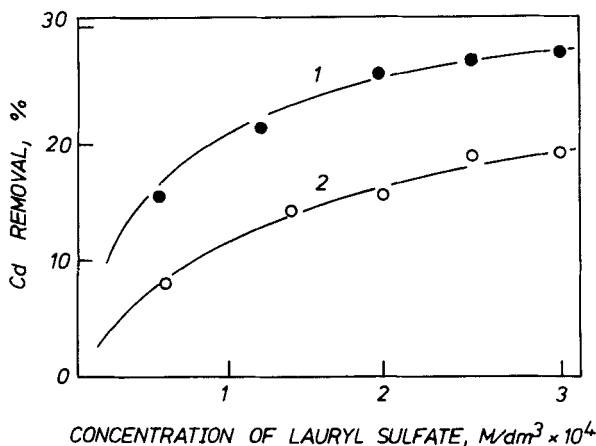
FIG. 2. Effect of sodium lauryl sulfate concentration on removal of Cd^{2+} (1, 0.05 M/dm^3 Na_2SO_4; 2, 0.3 M/dm^3 Na_2SO_4).

compound is abundant and very hydrated. Due to hydration of the polar groups of metal–alkyl sulfate complexes adsorbed on the bubble, a water sheath is formed. This phenomenon results by removing a certain amount of the liquid together with the metal in the foam fractionation process. This has a negative effect on the metal concentration in the foam.

Therefore, to better characterize the foam fractionation process, the removal of liquid from solutions was tested with the help of a single-bubble column (16). The results obtained are presented in Fig. 3. As can be seen, the increase of Na_2SO_4 concentration in the flotation solution results in a foam hydration increase, considerably reducing the solution volume in the column and worsening the quality of the foam concentrate.

In order to determine the surface properties of the flotation solutions containing lauryl sulfate, the surface electric potential of the solutions (ΔV) was measured. Figure 4 illustrates the changes of ΔV as a function of sodium sulfate concentration (Curve 1) and as a function of the collector concentration (Curve 2). As can be seen, the increase in electrolyte concentration to about 0.3 M/dm^3 decreases ΔV from about +40 to about −5 mV. This accounts for increased surface activity of the solutions with increased electrolyte concentration, and hence this indicates that sodium alkyl sulfate concentrates increasingly at the solution–gas interface. This figure also shows (Curve 2) that ΔV decreases with an increase of alkyl sulfate concentration, which also accounts for the increased surface activity of the solution. This results from increasing adsorption of the surface-active
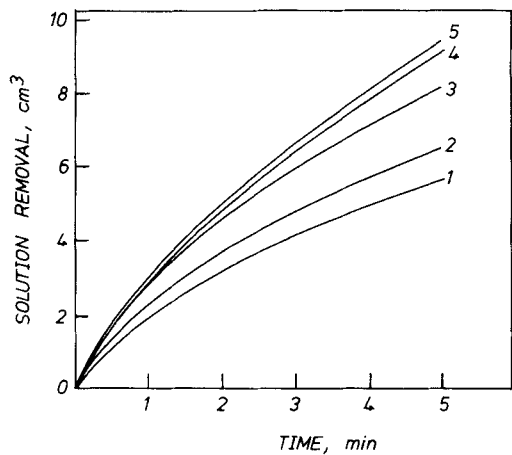
FIG. 3. Kinetics of liquid removal from Na_2SO_4 solution at different concentrations. Curves: 1, 0.001; 2, 0.01; 3, 0.1; 4, 0.2; 5, 0.3 in M/dm^3.
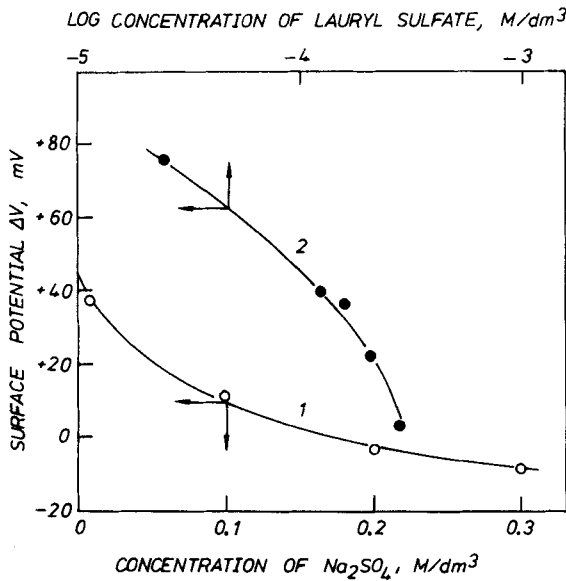

FIG. 4. Effect of sodium sulfate concentration (1) and sodium lauryl sulfate (2) on surface electric potential (ΔV) of the solution.

substance on the gas bubble with an increase of its concentration in the solution.

Next, the effectiveness of Cd^{2+} ion flotation by using sodium soaps (laurate and stearate) was studied. In Fig. 5 cadmium removal as a function of sodium sulfate concentration is presented. As shown in the figure, removal by stearate is about 10% higher than by laurate. In addition, in contrast to alkyl sulfate, Cd^{2+} removal increases to about 95% with an increase of electrolyte concentration by using soaps. Large amounts of cadmium soap precipitate are also observed in a very thin layer of the froth formation. It is therefore evident that in this process a considerable metal concentration in the froth is obtained, which is of great practical significance. A drawback to the use of such collectors is the weak frothing properties of the solution, and hence difficulties with the collection of the sublate follow. To improve the frothing properties of the solution, 0.004% of Tween 80 (polyoxyethylene sorbitan monooleate), a nonionic surface-active substance, was added to stearate. Figure 5 shows that the presence of Tween 80 improves Cd^{2+} foam separation owing to the formation of an abundant froth transporting the precipitate of cadmium stearate.

Next, the effectiveness of Cd^{2+} ion flotation was studied by using laurate and lauryl sulfate in the single-bubble flotation process with the simultaneous measurements of the hydration of gas bubbles. The results obtained are presented in Fig. 6. The single-bubble flotation carried out permitted determination of the percentage of cadmium removal and the average thickness of the water sheaths around gas bubbles (μ). The thickness of the water sheaths was calculated from the known volume of the liquid removed, the flow rate of nitrogen, and the number of bubbles which carried the liquid. From Fig. 6 it appears that if lauryl sulfate is used as a collector, Cd^{2+} removal decreases with an increase of electrolyte concentration, while the thickness of the water sheaths around the bubbles
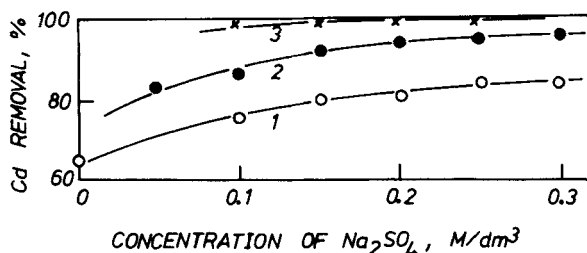

FIG. 5. Cd^{2+} ion flotation by using sodium laurate (1), sodium stearate (2), and sodium stearate with Tween 80 addition (3).
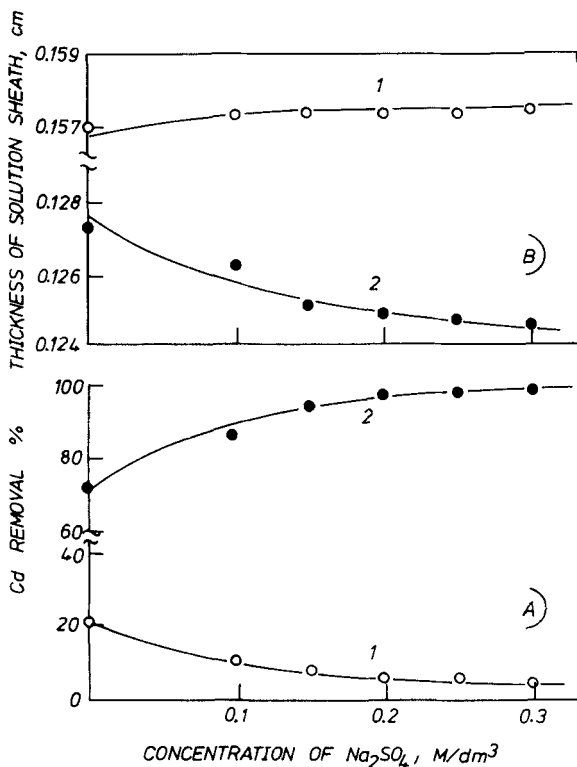
FIG. 6. (A) Effect of sodium sulfate concentration on Cd^{2+} removal in the single-bubble process. (B) Effect of sodium sulfate concentration on the liquid sheath around gas bubbles (μ). Curves: (1) by using sodium lauryl sulfate, (2) with sodium laurate.

increases. As a result, an increase of sodium sulfate concentration causes a decrease of cadmium concentration in the foam. In Fig. 6 the effectiveness of single-bubble flotation by using laurate is shown. It can be seen that Cd^{2+} removal increases with an increase of sodium sulfate concentration, but simultaneously the thickness of the water sheaths of gas bubbles decreases, which means that the hydration of the froth decreases. This leads to the conclusion that by using soaps in the ion flotation process, cadmium concentration in the froth is high and increases with an increase of electrolyte concentration in the solution.

DISCUSSION

The collectors applied for Cd^{2+} foam separation are ionic surfactants of the anionic type which are capable of dissociating and exchanging Na^+ for other metal cations:

$$Cd^{2+} + 2(RSO_4^-, Na^+) \rightleftharpoons 2RSO_4^-, Cd^{2+} + 2Na^+ \qquad (1)$$

$$Cd^{2+} + 2(RCOO^-, Na^+) \longrightarrow (RCOO)_2 Cd \downarrow + 2Na^+ \qquad (2)$$
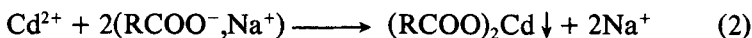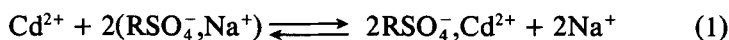
The products of Reactions (1) and (2) are removed from solution on gas bubbles. Karger (21) and Grieves et al. (22, 23) consider soluble ionic–surfactant–metal ion complexes as ion pairs and they have found an analogy between foam fractionation and ion exchange. According to their suggestion, the product of Reaction (1), i.e., cadmium lauryl sulfate, can be recognized as being in the form of a hydrated ionic pair $(2RSO_4^-, Cd^{2+})_{(H_2O)_n}$. Assuming that cation exchange is not complete, it is expected that sodium lauryl sulfate is in the form of the hydrated ionic pairs $(RSO_4^-, Na^+)_{(H_2O)_m}$, i.e., an inactive ion pair of the collector is in equilibrium with cadmium lauryl sulfate. Such an equilibrium condition is possible, particularly in the case of the cations studied by us, because the combinations of both metals with alkyl sulfate are completely soluble in water and variously hydrated. Accordingly, the adsorbed-hydrated layer of gas bubbles has a mixed structure made up of sodium alkyl sulfate and cadmium alkyl sulfate in the form of an ion pair.

The equilibrium conditions of Reaction (1) are characterized by the equilibrium constant

$$K = \frac{[2RSO_4^-, Cd^{2+}][Na^+]^2}{[Cd^{2+}][RSO_4^-, Na^+]^2} \qquad (3)$$

The efficiency of Reaction (1) can be expressed as

$$\frac{[2RSO_4^-, Cd^{2+}]}{[Cd^{2+}]} = \frac{K[RSO_4^-, Na^+]^2}{[Na^+]^2} \qquad (4)$$

The effectiveness of foam fractionation can be expressed by the distribution coefficient of cadmium between the foam phase and the residual solution phase. The left side of Eq. (4) presents the distribution coefficient of cadmium. From this it can be seen that the efficiency of Reaction (1), i.e., the efficiency of foam fractionation of cadmium, increases with an increase in the value of the reaction constants (K) and collector concentration.

However, the increase of sodium cation concentration causes a decrease in the effectiveness of cadmium foam fractionation.

Substituting α for the left-side of Eq. (4), we obtain

$$\log \alpha = \log K + 2 \log [RSO_4^-, Na^+] - 2 \log [Na^+]$$

The last equation shows that $\log \alpha$ depends linearly on $\log [Na^+]$, and the slope of these linear functions equals 2, i.e., it is equal to the charge of cadmium cations.

Analysis of Figs. 1 and 2 shows a high coincidence of the above theoretical conclusions with the results obtained for the foam fractionation yield. As the Na^+ concentration in the initial solution increases, which results from sulfate or nitrate, the effectiveness of Cd^{2+} binding by RSO_4^- decreases and the equilibrium of Reaction (1) shifts to the left and the gas bubble–solution interface is enriched with sodium alkyl sulfate at the expense of cadmium alkyl sulfate. This is the reason for decreasing Cd^{2+} removal in the foam fractionation process with increasing electrolyte concentration. The slope of the curve of foam fractionation from sulfate solutions is twice as large as that of the foam fractionation curve from nitrate solutions, because at equal molar concentrations of both electrolytes, twice as many Na^+ are in sulfate as in nitrate solutions. This cation competition was reported for foam fractionation of Co^{2+}, Ni^{2+}, and Cu^{2+} with lauryl sulfate in our previous studies (24, 25), by Rubin and Johnson (26) for Fe^{3+}, and by Ferguson et al. (1) for Pb^{2+} and Fe^{3+}. The same trend has been observed by Walkowiak and Grieves (14, 15) for anions (simple ones and complex metal anions with chloride or cyanide) with surfactant cations in foam fractionation.

The enrichment of the gas bubble–solution interface with sodium alkyl sulfate also results in increased thickness of the water sheath around the bubble and, consequently, in increased foam hydration. From the above it appears that the changes of the function μ vs sodium sulfate concentration in the presence of lauryl sulfate are incompatible with predictions made from the Debye-Hückel theory, where a higher ionic strength leads to a thinner ionic atmosphere, which should lead to thinning of the water sheath around the gas bubble. The same problem was discussed by Wilson (27, 28).

Because the expected relationship does not happen, it is likely that besides compression of the electric double layer, the added inert electrolyte causes specific adsorption of the collector which directly effects the increased hydration of gas bubbles. At high Na_2SO_4 concentration the charge of RSO_4^- anions in the adsorption layer of gas bubbles is more rapidly neutralized by Na^+ the higher the concentration of salt. Further-

more, at a proper concentration of Na^+ in the solution, the coulombic repulsion forces in the adsorption layer can be completely eliminated. Accordingly, a closer packing of hydrated RSO_4^-,Na^+ ion pairs takes place in the surface layer (ΔV decreases with an increase of salt concentration). This has been shown by Zwierzykowski (29). As a result, the water sheaths of gas bubbles become more stable and thicker. Hence, the cadmium concentration in the foam is low. Therefore, the practical use of alkyl sulfates for foam fractionation of metal cations is unsatisfactory. However, the removal of surfactants is possible by foaming.

In further studies, sodium soaps were used as collectors, which with Cd^{2+} form cadmium soaps of low solubility according to Reaction (2). The precipitate is sufficiently hydrophobic so that it is adsorbed on gas bubbles and is removed from the sulfate solution in the ion flotation process. Cadmium laurate removal from the solution prevents the exchange of Cd^{2+} cations from the precipitate (sublate) on Na^+ cations from the solution. Therefore, it does not appear from the experiment that an increase in the ionic strength of the solution caused by an inert electrolyte would increase the solubility of a low-soluble ionic precipitate, as predicted by the Debye-Hückel theory. It can even be assumed that due to a stronger Na^+–water dipole (a higher Na^+ hydration) interaction than that of cadmium laurate and water dipoles, a salting-out effect of laurate occurs because with increasing inert electrolyte concentration, cadmium removal increases and hydration of gas bubbles decreases. Thus, the use of soaps in practical flotation seems to be very promising.

It appears from the experimental data that the mechanism and effectiveness of the cadmium removal process result from the nature of the metal ion (colligend)–collector product. Both collectors (sodium laurate and sodium lauryl sulfate) can be treated as soluble ion exchangers. The product (cadmium lauryl sulfate) formed in the exchange reaction is totally soluble. It can therefore be called a hydrated ion pair $(2RSO_4^-,Cd^{2+})_{(H_2O)_n}$. Cadmium removal with lauryl sulfate occurs by foam fractionation. The presence of an inert salt has a negative effect on cadmium foam fractionation. However, a cadmium laurate $(RCOO)_2Cd$ formed in the exchange reaction is a precipitate of low solubility. Thus, cadmium removal by sodium laurate occurs by the ion flotation process. The presence of the electrolyte in the concentration range studied positively effects the effectiveness of cadmium ion flotation.

In both foam fractionation and ion flotation processes, changes of cadmium removal and hydration of gas bubbles as a function of the salt concentration are not parallel. This supports the idea that cadmium is removed through electrostatic interaction of metal ions and the collector according to Reactions (1) and (2), and not only by cadmium ion removal in the hydration sheath of a gas bubble.

However, it should be remarked that the efficiency of the collector–Cd^{2+} ion reaction is not equivalent to that of foam separation because, apart from chemical parameters, the removal is also affected by physical processes such as the process time and the gas flow rate. The correlation of reaction efficiency with cadmium removal requires further studies.

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