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Studies on the Separation of Cadmium from Solutions by Foam Separation. III. Foam Separation of Complex Cadmium Anions

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Abstract

The effects of thiocyanate and iodide concentrations, acidity and nature of the acid, and various alcohols on the removal of cadmium and liquid in the foam separation process were studied. Moreover, the surface tension and electric surface potential of some solutions were measured. The results of foam separation and changes of the surface properties of the solutions were interpreted on the basis of the ratio of concentrations of cadmium complexes and the exchange of the collector bromide counterions for the ligand anions, complex cadmium anions, or acid anions.

INTRODUCTION

Foam separation is an example of the practical utilization of adsorption at the gas–solution interface to separate metals from solutions. In previous papers (*1*) foam separation of cadmium cations and hydroxide from neutral electrolyte solutions was discussed. From the review of publications made on that occasion it appears that foam separation of cadmium in the form of complex anions has not been studied extensively. This problem was the subject of studies of Walkowiak et al. (*2, 3*). The objective of those investigations was the selective removal of Zn, Hg, Cd, and Au by foam fractionation from acidic chloride and cyanide solutions using the cationic surfactant hexadecyltrimethylammonium chloride. The present studies concern cadmium flotation under conditions affecting the formation of

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anionic metal complexes. It is known from the literature (*4–8*) that many anions, particularly thiocyanate and iodide, form complex anions of the type $(CdL_4)^{2-}$ with cadmium. Intermediate forms occur in equilibrium with the final forms in concentrations dependent on the concentration of excess ligand; a number of other factors also stabilize the complex in the solution. These conditions also affect the structure of the gas–solution interface and the surface properties of the solution. The relationship between the interaction of ions in the solution and surface phenomena has been little known, so great difficulties exist in the theoretical description of the course of cadmium ion flotation. The present studies were undertaken to further elucidate this problem.

EXPERIMENTAL

The initial aqueous solutions were prepared with double distilled water. The solutions used contained 10^{-4} M/dm^3 of Cd^{2+} ions which came from analytically pure cadmium sulfate produced by POCH Gliwice. Of the same purity and origin were the other reagents: potassium thiocyanate, potassium iodide, acids, and alcohols.

Analytically pure cetyltrimethylammonium bromide, used as the collector, was produced by Chemapol Praha. The collector concentration was 2×10^{-4} M/dm^3.

Foam separation was carried out in a multibubble apparatus. The apparatus was a glass column 25 cm high and 200 cm^3 in volume with a G-3 sinter (15–40 μm nominal porosity) in its bottom part. Nitrogen was passed at a flow rate of 25 cm^3/min for 10 min. The effectiveness of flotation was calculated on the basis of determinations of cadmium in the initial suspension and residual bulk flotation suspension. The determinations were preceded by decomposition of the cadmium and collector complexes. For this purpose a sample of the suspension was evaporated with concentrated nitric acid, and then ammonium nitrate was added for complete combustion of the collector. The residue was dissolved in water, and cadmium was determined by complexometric titration with EDTA (*8, 9*).

The volume of the liquid removed with the bubbles was determined by using a monobubble apparatus described elsewhere (*10*). First, the change in the volume of the liquid removed from suspensions of various concentration of thiocyanates and iodides and in the presence of cadmium or without cadmium was determined in relation to the time of gas flow. On this basis the kinetic curves of liquid removal were plotted. Then, from these curves the volumes of the liquid removed after 5 min from the beginning of the process were read.

The surface tension of the suspensions was measured with a Du Nouy tensiometer, the ring of which was made from platinum wire.

Electric surface potential (ΔV) was measured according to a literature method (*11, 12*). The apparatus used is also described in the literature (*11, 12*). The ionization methods was used, with ^{239}Pu as the source of α-particles. The activity of the source was 10 mCi. The potential value was measured in the following systems: V_1 in the system calomel electrode/basic solution—air/Au; V_2 in the system calomel electrode/flotation suspension—air/Au. It should be additionally clarified that after introducing the collector into the solution containing Cd^{2+}, SCN^-, or I^-, precipitation of ammonium salt sediment followed. As a result of this, the electric (adsorption) surface potential (ΔV) was the difference between the potential (V_2) of the flotation suspension and the potential (V_1) of the basic cadmium sulfate solution at 10^{-4} M/dm^3 concentration.

RESULTS

The effect of potassium thiocyanate and potassium iodide on cadmium removal are presented in Fig. 1 (Curves 1–3); the pH of the solutions was about 6. The effectiveness of flotation from thiocyanate suspensions is characterized by two curves. One curve is related to determinations of cadmium in suspensions in which complex thiocyanate–cadmium anions and collector compounds were decomposed. The other curve is related to determinations carried out without decomposition of complex anions and collector compounds. As is known (*8, 9*), versenate reacts only with metal cations, forming stable compounds. Therefore, cationic cadmium forms were determined without decomposition of unfloated metal–thiocyanate (iodide)–collector compounds. Therefore, only the first curve illustrates true removal. The area between the curves illustrates the amount of cadmium which may still be removed but has not been floated, probably because of inadequate physical parameters of the flotation process such as time or gas flow rate.

From Fig. 1 it can be seen that increasing the concentration of thiocyanate or iodide to about 0.3 M/dm^3 causes increased cadmium removal. In a suspension of this salt concentration there is over a thousandfold excess of thiocyanate or iodide relative to the cadmium concentration. Metal removal from thiocyanate media under these conditions reaches about 45% (about 60% from iodide media). Further increase of salt concentration causes a decrease in cadmium removal.

The results of determinations of the amount of cadmium in solutions of various thiocyanate concentrations without flotation are presented in Fig. 1, Curve 4. As can be seen, the amount of cadmium determined decreases

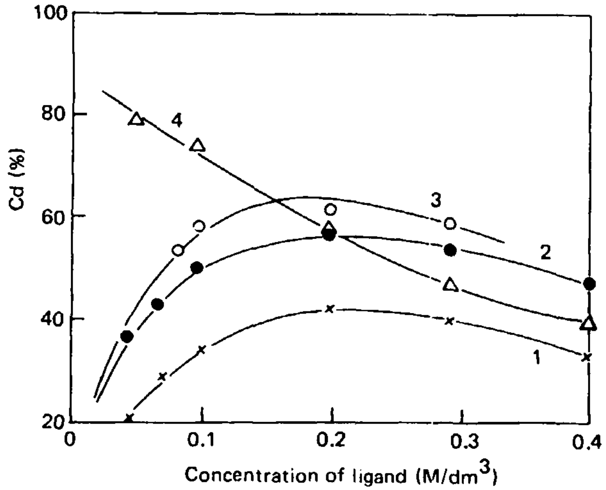

FIG. 1. Effect of potassium thiocyanate and potassium iodide on cadmium removal (Curves 1–3) and on the results of determinations of the amount of cadmium in solutions (Curve 4). Curves 1, 2, and 4: KSCN. Curve 3: KI.

with increased salt concentration. This is explained in terms of increasing amounts of thiocyanate–cadmium complexes. However, cadmium removal increases proportionally to the amount of complexed metal only in the concentration range of thiocyanate from 0–0.3 M/dm^3.

Apart from cadmium removal, the extent of enrichment of the metal in the foam is another important parameter which determines flotation effectiveness. It is controlled by the volume of liquid removed together with the sublate on the bubble. Figure 2 illustrates the effect of thiocyanate and iodide concentrations on liquid removal. It can be seen that the volume of this collapsed foamate decreases as salt concentration increases. When salt concentration increases from 0.05 to 0.3 M/dm^3, the removal of the solution from thiocyanate medium in the presence of cadmium decreases from 16 to 7 cm^3 (from 16 to 1 cm^3 from iodide medium). Thus it appears that less liquid is removed from iodide suspensions than from thiocyanate ones. Moreover, liquid removal is lower in the presence of cadmium than without it.

The surface properties of flotation suspension are illustrated by Figs. 3 and 4. Figure 3 presents the influence of thiocyanate and iodide concentrations on the surface tension (σ) and surface electric potential (ΔV) of the suspensions. The values of both parameters grow in parallel with increasing salt concentration. As thiocyanate concentration increases from 0.05 to 0.3 M/dm^3, σ (the surface tension) increases from 47.5 to 53 dyn/cm, whereas

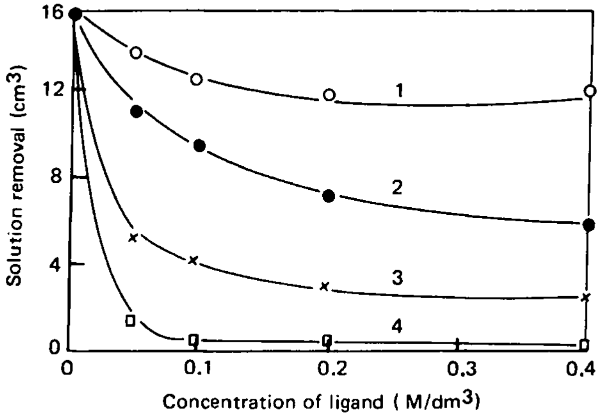

FIG. 2. Effect of thiocyanate and iodide concentrations on liquid removal. Curves 1 and 2: KSCN. Curves 3 and 4: KI. 1, 3–without Cd; 2, 4–present Cd.

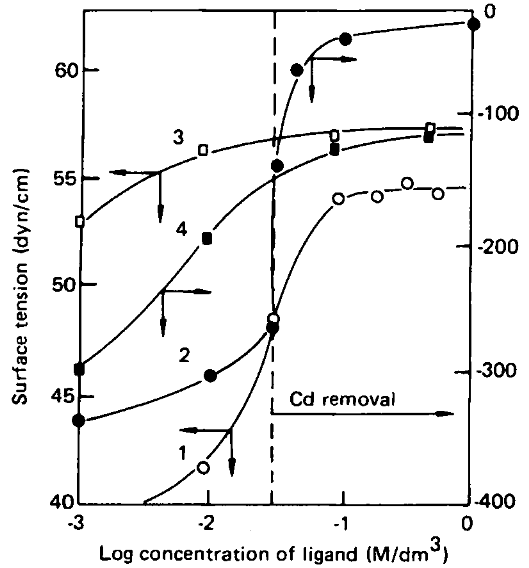

FIG. 3. Influence of thiocyanate and iodide concentrations on the surface tension and electric surface potential of suspensions. Curves 1 and 2: KSCN. Curves 3 and 4: KI.

ΔV increases from -260 to -20 mV; at the same iodide concentration, σ increases from 55 to 56 dyn/cm, and ΔV from -130 to -110 mV.

Figure 4 illustrates changes of ΔV in relation to the composition of the solution. The amounts of thiocyanate, collector, methanol, and cadmium used were 0.2 M/dm^3, 2×10^{-4} M/dm^3, 2%, and 10^{-4} M/dm^3, respectively. The flotation suspension contained these four components. As seen from the figure, ΔV of different solutions changes as follows: Cd, collector, methanol < Cd, methanol < Cd, KSCN, collector, methanol < Cd, KSCN, methanol. The surface-active components of the solutions are the collector and methanol. Accordingly, the lowest ΔV value is demonstrated by the solution containing these two components with cadmium. The minimum ΔV value is -380 mV. From an analysis of the figure it can be estimated that the contribution of the collector to decrease ΔV is three times larger than that of methanol. However, in the presence of thiocyanate, ΔV is the highest—about -10 mV. No significant changes of ΔV are observed to be caused by changes of the other components of the solution.

The acidity of the medium and the nature of the acid are significant factors affecting the form of ions and compounds in the solution. The effect of the nature of the acid (HA) on cadmium removal from suspensions at a thiocyanate concentration equal to 0.2 M/dm^3 and an acid concentration equal to 0.2 M/dm^3 is presented in Fig. 5. The measured pH of suspensions of perchloric, hydrochloric, nitric, and sulfuric acids was 1.15, that of phosphoric acid was 1.80, and that of acetic acid was 2.83. As shown, the presence of acid decreases the removal of cadmium. Cadmium removal in the presence of various acids increases in the following sequence: $HClO_4$ < HCl < HNO_3 < H_2SO_4 < H_3PO_4 < CH_3COOH < without HA. This series corresponds to the decrease of acid strength expressed by pK_{HA} (*13*).

The collector is prepared as a solution in an organic solvent which is

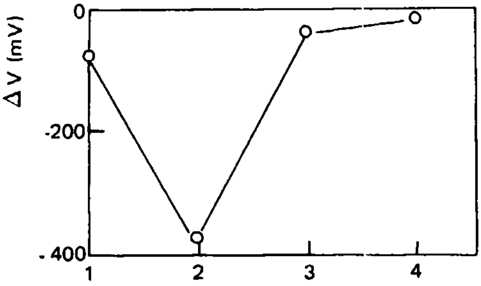

FIG. 4. Changes of electric surface potential in relation to the composition of the solutions. 1: Cd and methanol. 2: Cd, methanol, and collector. 3: Cd, methanol, collector, and KSCN. 4: Cd, methanol, and KSCN.

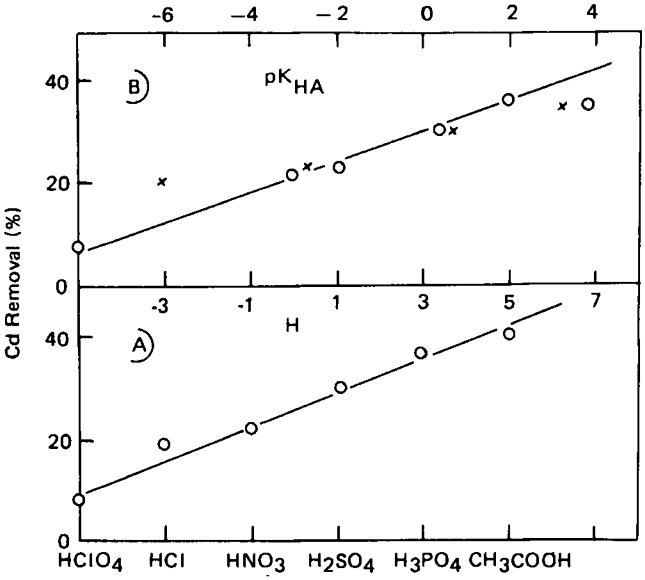

FIG. 5. Effect of nature of the acid on cadmium removal from thiocyanate suspensions: (O) pK_{HA}, (X) H.

miscible with water. This condition is met by lower alcohols. However, they affect the reaction course in the solution, and probably the flotation effectiveness at the same time. The experimental results concerning this problem are summarized in Fig. 6. Alcohol concentration was 2%, and that of thiocyanate 0.2 M/dm^3. From the figure it appears that increasing the length of the hydrocarbon chain of alcohols from C_1 to C_4 improves the removal from 40 to 65%. In the same figure, changes of the surface tension and surface electric potential of suspensions due to different alcohols are also illustrated. These parameters, in constrast to cadmium removal, are inversely proportional to the length of hydrocarbon chain of alcohol. When the alcohol is changed from C_1 to C_4, σ decreases from 55 to 50 dyn/cm, and ΔV from -10 to -210 mV.

DISCUSSION

Effect of Salt Concentration

The metal in the form of ions present in solution may undergo concentration in the area of the solution–gas interface only if it reacts with

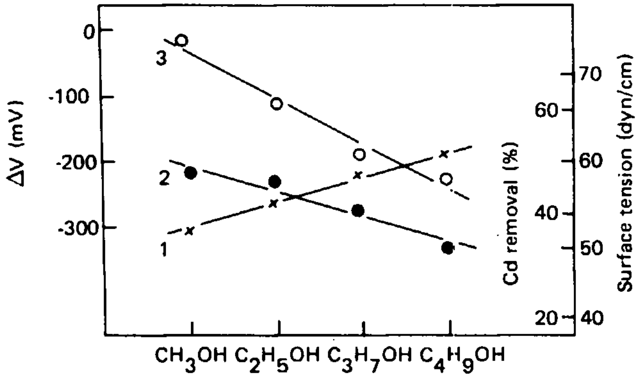

FIG. 6. Flotation effectiveness (Curve 1), σ and ΔV (Curves 2 and 3) of suspensions in the presence of various alcohols.

the chemical reagents to produce a hydrophobic compound. From the results obtained it appears that such a role is played by cetyltrimethylammonium bromide. It is a cationic surface-active substance and its hydrophobic chains are included in the composition of the cation $C_{17}H_{33}N^+(CH_3)_3$. Sublate is formed owing to the binding of counterions containing cadmium by this cation, which is adsorbed on gas bubbles and is removed from the suspension.

Cadmium Removal

It can be seen from Fig. 1 that the removal of cadmium in the foam increases with increasing concentration of thiocyanate or iodide. If we assume the least complicated mechanism of collector interaction with the metal ion, i.e., electrostatic, it can be concluded that the removed cadmium is present as the complex anion. However, from the literature (*4–8*) it is known that several compounds $(CdL)^+ \rightleftarrows (CdL_2) \rightleftarrows (CdL_3)^- \rightleftarrows (CdL_4)^{2-}$ are formed due to the reaction between potassium thiocyanate or potassium iodide and cadmium cations by a stepwise exchange of water molecules of the cation $(Cd(H_2O)_6)^{2+}$ for ligands forming complex metal anions $(Cd(H_2O)_{(6-n)}L_n)^{(2-n)}$.

The relative amounts of the individual complex formed depend on the excess concentration of thiocyanate or iodide in relation to cadmium concentration. When the excess concentrations are high, essentially only anions $(CdL_4)^{2-}$ are formed (*4–8*).

It is known that versenate (sodium salt of ethylenediamineacetatic acid, EDTA) reacts with cadmium cations to form stable complexes (*5, 9*). The stability of these complexes is characterized by stability constants: CdL = 16.46, CdHL = 19.4. However, the stability constants of thiocyanate–cadmium complexes are CdL = 1.4, CdL_2 = 1.88, CdL_3 = 1.93, CdL_4 = 2.38 (*5, 9*). With increased concentration of thiocyanate anions the concentration of relatively stable thiocyanate complexes tends to increase. Therefore, when thiocyanate concentration increases (in the presence of collector), versenate complexing simultaneously decreases. This confirms an earlier conclusion that Curve 4 in Fig. 1 illustrates the effect of thiocyanate concentration on the amount of cadmium bonded in a complex anion. As regards the correlation of increased cadmium removal with increased extent of the metal complexation (which results from Fig. 1), the relationship between removal and the formation of cobalt and nickel thiocyanate complexes published earlier by Jurkiewicz and Waksmundzki (*14*) and the results of cadmium, zinc, mercury, and gold flotation from chloride and cyanide solutions published by Walkowiak et al. (*2, 3*) have been confirmed.

According to literature data (*4, 8*), thiocyanate–cadmium complexes are weaker than iodide–cadmium ones, which possess the following stability constants: CdL = 2.28, CdL_2 = 3.92, CdL_3 = 5.0, CdL_4 = 6.1. This is likely to cause a higher concentration and removal of cadmium from iodide media than from thiocyanate suspensions.

Given the conditions $[SCN^-] \gg [Cd^{2+}]$ or $[I^-] \gg [Cd^{2+}]$, not only complex anions of cadmium (Reaction 1) but also thiocyanate or iodide anions may be attached by the collector (Reaction 2).

$$2(R_4N^+,\ Br^-)_{(H_2O)_n} + Cd^{2+} + mL^- \longrightarrow (R_4N)_2(CdL_4)\downarrow$$
$$+\ (m-4)L^- + 2Br^- + nH_2O \qquad (1)$$

$$2(R_4N^+,\ Br^-)_{(H_2O)_n} + Cd^{2+} + mL^- \longrightarrow 2R_4NL\downarrow + (CdL_4)^{2-}$$
$$+\ (m-6)L^- + 2Br^- + nH_2O \qquad (2)$$

Hydrated ion pair (collector) Hydrophobic sediment

As regards this problem, Grieves et al. (*15, 16*) have estimated the following affinity series: $SCN^- > Br^-, I^- > Br^-$. This can be described as competition between ligand and complex anions to combine with the collector. The competition of various anions with chloride and cyanide complex anions of cadmium and other metals for hexadecyltrimethylammonium collector was studied by Walkowiak et al. (*2, 3*).

This probably takes place during foam separation from suspension at concentrations of the ligand above 0.3 M/dm^3, because cadmium removal decreases, although the percentage of complexed metal increases (Fig. 1).

However, it should be stressed that salt introduced into solution of cadmium and collector ions does not only provide the ligand but also causes salting out of the reaction product. The literature data concerning chromatography, extraction, and ion exchange (*17–19*) confirm the exchange of bromide counterions of alkylammonium salt for thiocyanate or iodide counterions. This is connected to the trend of decreasing hydration energy with increasing anion radius.

Liquid Removal (hydration of gas bubbles)

We assume that $(R_4N)_2(CdL_4)$ and coprecipitated R_4NL are the materials removed on the gas bubbles. From Fig. 2 it can be seen that they change gas bubble hydration. The volume of liquid removed decreases as the amount of cetyltrimethylammonium salt increases in the following sequence: $(R_4N^+, Br^-)_{(H_2O)_n}$ > R_4NSCN > $(R_4N)_2Cd(SCN)_4$ > R_4NI > $(R_4N)_2Cd(I)_4$. Because of the complete solubility of alkylammonium bromide, it was assumed to be present as hydrated ion pairs. Other alkylammonium salts, however, constitute various slightly soluble hydrated precipitates. Therefore the following factors which tend to change the hydration of the collector compounds should be taken into consideration.

In the first case hydrated bromide counterions (Reaction 2) are replaced by large and less hydrated thiocyanate or iodide counterions. In the second case the reason is more complex because cadmium complexing itself causes destruction of the hydration shell of the ion, forming a large, slightly hydrated anion, which in turn combines with the collector and decreases its hydration, forming hydrophobic alkylammonium compounds (Reaction 1). Because of better metal complexing by iodide than by thiocyanate ligands, hydration of bubbles in iodide medium is lower than in thiocyanate medium. Thus the results presented confirm the general rule that hydration decreases with the increasing dimension of the complex ion forming the compound and with a decrease of the dipole moment of the compound (*18–21*).

Change of Surface Properties of the Solution

Some quantity of liquid is removed together with sublate on gas bubbles in the flotation process. This fact indicates that the floated substance, gathering in the liquid–gas interface area, is separated together with the surface layer of liquid. The sublate thus remains in its liquid phase. It seems, therefore, that metal removal is characterized by changes of the solution surface properties. It can be seen in Fig. 3 that σ and ΔV increase with increasing thiocyanate or iodide concentration. Cadmium removal and the rate of metal complexing increase analogously, but liquid removal decreases.

In the flotation solution, bromide counterions of the collector are exchanged for iodide, thiocyanate counterions, or complex cadmium anions (Reactions 1 and 2). This is according to the principle that large and less hydrated anions (SCN^-, I^-, $(CdL_4)^{2-}$) show a greater affinity for alkylammonium cation than smaller anions (Br^-) which are strongly hydrated (*18–21*). The product of these reactions is a hydrophobic precipitate of low solubility. The collector thus leaves the solution in the form of precipitate $(R_4N)_2(CdL_4)$ or R_4NL, and it disappears from the surface layer. Therefore, σ and ΔV values increase, approximately to the values characteristic for the solution of inorganic ions without collector (Figs. 3 and 4). Thus the changes of σ and ΔV reflect changes of the solution surface properties which have been caused by the reaction of the collector cations with anions present in the flotation suspension. These data confirm the observations published elsewhere (*22*). Although the amount of removed cadmium also depends on the amount of the product of this exchange reaction, there is not a direct correlation between precipitate removal and σ or ΔV. This is indicated by the fact that cadmium removal increases, whereas collector adsorption expressed as the inverse of σ and ΔV decreases, as well as by the identity of suspension and solution after filtering off sublate precipitate. These data account for the dependence of σ and ΔV values on the amount of soluble collector. There is, however, a direct relationship between σ or ΔV and liquid removal because it is mainly the adsorbed soluble collector molecules which are the reason for bubble hydration, and not hydrophobic precipitate. Increased σ and ΔV account for the decreased adsorption of these molecules which is connected with decreased hydration of gas bubbles.

Influence of the Nature of Acid

In the presence of the acids ($[HA] = [SCN^-] = 0.2$ M/dm^3), cadmium removal increases in the following way: $HClO_4 < HI < HNO_3 < H_2SO_4 < H_3PO_4 < CH_3COOH <$ without HA (Fig. 5). To make this clear, acid strength (pK_{HA}) was correlated with removal. Figure 5(B) shows that cadmium removal decreases proportionally to acid strength. It can be described by

$$R_{HA} = R_0 + a(pK_{HA} - pK_0) \qquad (3)$$

where R_{HA} is the removal from suspension in the presence of an acid (HA) and a is the slope of this linear function. Since the nature of the acid was the changeable parameter in the course of the investigation, cadmium removal from the medium without acid, R_0, may be assumed as a comparative point; then pK_0 can be found by extrapolation of this linear function up to the level R_0. This suggests that a strong acid introduced into thiocyanate medium causes a decrease in the number of complex metal anions which are able to bind with the collector. This probably results from the fact that the presence of a strong acid weakens or even suppresses dissociation of thiocyanic acid proportionally to the difference of the acid strength, and therefore free ligands for cadmium complexing diminish in the solution.

It is also possible for acid anions to be attached to the collector according to the order of their strength (*18, 19, 23*) in place of thiocyanate–cadmium complex anions. This reduces cadmium removal in a simple way.

The competitiveness of anions of acid depends on acid strength and the solubility of the collector salt. Among various salts, R_4NClO_4 perchlorate is least soluble. Therefore, precipitation of white alkylammonium perchlorate is observed. Due to the fact that a part of this collector ceases to be effective in binding to thiocyanate–cadmium anions, cadmium removal is lowest in the presence of $HClO_4$.

It is therefore difficult to determine unequivocally the reason for decreased cadmium removal in the presence of acid, because it is the result of various processes and of the properties of compounds of the collector with anions. There is still one impediment to the unequivocal determination of the flotation mechanism. Figure 5(B) shows that there exists a direct correlation of removal with H, the so-called Edwards nucleophilicity function of anions (*24*). This can be similarly presented by Eq. (3). On this basis the collector reactions can be considered not only as anion exchange but also as an attachment reaction (*23–26*). There is probably a complex of mechanisms, and the domination of one of them depends on the solution conditions.

Cadmium Removal in the Presence of Various Alcohols

The development of a proper method of preparing and introducing the collector into the solution is one of the problems in conducting foam separation. A number of experiments have been made to study this problem, the results of which are presented in Fig. 6. From Fig. 6 it appears that each of the values measured can be expressed by

$$X(n) = X(n_0) + C_X \cdot (n - n_0) \tag{4}$$

where $X \in \{R, \sigma, \Delta V\}$, $n \in \{1, 2, 3, 4\}$ determines alcohol (number of carbon atoms in alcohol), whereas $(n_0, X(n_0))$ is the reference point (reference alcohol). From the figure it appears that the series of removal R (Curve 1) increases as follows: methanol < ethanol < propanol < butanol (the slope C_R is positive). The other values (σ, ΔV) change inversely proportionally with an increase in the number of carbon atoms in the alcohol ($C_{\sigma,\Delta V}$ shows negative values).

The dielectric constant of the alcohol and of its water solution decreases with the chain length of the alcohol; cadmium removal can be expressed as a function of the dielectric constant. From the above it appears that cadmium removal decreases as the dielectric constant increases. Taking into consideration the influence of alcohol on removal, attention should be drawn to its possible effect on two principal stages of flotation: (a) metal complexing and the formation of collector compounds; (b) change of the solution–gas interface structure. As regards the former stage, it is known that complexes are formed with greatest difficulty in aqueous solutions (*27*). Formation of complexes in alcohol solutions is easier, and it increases with an increase in the number of carbon atoms in an alcohol. It is aided by the presence of alcohol in the solution, which is a dehydrating factor.

Complexes $(Cd(H_2O)_{(6-n)}L_n)^{(2-n)}$ are known to be gradually formed from $(Cd(H_2O)_6)^{2+}$. Thus, all the above equilibrium complexing constants undergo changes which, generally speaking, are connected with the chemical properties of the alcohol. In addition, the presence of alcohol in solution decreases the dielectric constant of the solution proportionally to the amount of alcohol and number of carbon atoms in the alcohol. This affects the stabilization of complex anions of cadmium and collector compounds, because the work needed to push apart two ions of different charges is inversely proportional to the dielectric constant of the medium. Dehydration and stabilization of compounds have a positive effect on cadmium removal. From the earlier results (Figs. 3 and 4) it may be concluded that if alcohol affected only the stability of thiocyanate complexes and their sublates with cetyltrimethylammonium collector, then ΔV and σ of the suspension would increase from methanol in the direction of butanol. However, as seen from Fig. 6 (Curves 2 and 3), ΔV and σ of the solutions decrease with an increasing number of carbon atoms in the alcohol. This indicates that some quantity of alcohol molecules is adsorbed together with the sublate at the flotation suspension–gas interface. As a result, the amount of foam may increase. However, this adsorption may also result in displacing the sublate molecules by alcohol molecules from the flotation suspension–gas interface.

The results obtained lead us to propose that the method of foam separation may be helpful in learning the structure of the solution and in studying interface phenomena, and it may be practical for removing the metal from solution. The conclusions drawn from this paper are supported by a variety of experimental results, and their verification will be the subject of further studies.

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