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# Foam Separation of Metals from Aqueous Thiocyanate/Alcohol Solutions

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## Abstract

Thiocyanate complexes of cobalt were floated in the presence of various alcohols and those of cadmium in the presence of propanol. The effectiveness of the foam separation of thiocyanate complexes by means of cetyltrimethylammonium bromide decreased in the sequence methanol < ethanol < propanol and with increasing concentration of alcohol over a certain concentration range. Maximum removal was obtained at different concentrations of alcohols (about 17, 14, and 10%, respectively) but at an equal dielectric constant of aqueous-alcohol solutions (about 73.5). In addition, collector removal, solubility of the sublate, and the change of the surface properties ($\delta$ and $\Delta V$) of the flotation suspensions were studied. The effectiveness of foam separation of complex metal anions and collector is connected to the solubility of the sublate and competitive adsorption of alcohol at the suspension/gas interface.

## INTRODUCTION

The basic reaction of foam separation is the formation of sublate. To make the course of the reaction most effective, appropriate preparation of the collector solution is required in which individual collector molecules are protected from micellization. Therefore, the collector should be prepared in a solution of an organic solvent which is mixed with an aqueous solution. This condition is satisfied by lower alcohols of hydrocarbon chain length $C_1$–$C_3$.

Pinfold (*1*) reports that "recent measurements have shown, however,

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that micelles break down rapidly, and their presence may not, in fact, be detrimental. It is convenient to continue this practice nonetheless as many of the collectors used are not very soluble and it is necessary to maintain them in solution until they can come in contact with colligend ions.

Therefore, provided that the collector is soluble, alcohol is not really needed and was, in fact, omitted in some studies by Grieves et al. (*2*). Omission is advisable where possible, as it has been shown by Davis and Sebba (*3*) and Kuzkin and Semeshkin (*4*) that too much alcohol suppresses flotation.

Skrylev et al. (*5*) stated that removal of nickel, cobalt, and copper laurates decreased monotonically with increasing butanol and glycerin concentrations; on the other hand, with increasing ethanol and acetone concentrations the removal decreased at first and then increased. Moreover, according to Skrylev et al. (*6*), the effectiveness of foam fractionation of dimethyloctadecylbenzylammonium chloride in the presence of low concentrations of alcohols (propanol, butanol, amyl alcohol) increased, but in the presence of high concentrations of alcohols the effectiveness decreased.

Shakir (*7*) came to the conclusion that the removal of uranium from carbonate solutions decreased significantly with an increase of ethanol concentration.

In a previous paper (*8*) it was found that the effectiveness of foam separation of complex cadmium anions from a medium containing 2% alcohols increased with an increasing number of carbon atoms (to $C_4$) in the alcohol. However, under these conditions the surface tension and adsorption potential of the flotation medium decreased. The results of these studies suggest that there exist many problems of foam separation which should be elucidated on the basis of further experiments.

The main problem is to determine the influence of higher alcohol concentration in aqueous solutions on sublate solubility, on the competitive adsorption of alcohol and sublate on gas bubbles, as well as on the formation of colligend ions (complex metal anions). The first and second phenomena may negatively affect foam separation; however, it cannot be said whether and at what concentration of alcohol they take place, particularly because the third phenomenon, i.e., metal complexing, has a positive effect on the removal of complex metal ions (*8–11*).

## EXPERIMENTAL

The initial aqueous solutions were prepared with double distilled water. The solutions used contained $10^{-4}$ mol/dm$^3$ of analytically pure cobalt chloride or cadmium sulfate produced by POCh Gliwice. The other reagents, potassium thiocyanate and alcohols, were of the same purity and origin. The alcohols were dehydrated by silica gel before use. Analytically pure cetyltrimethylammonium bromide, used as the collector, was produced by Chemapol Praha. The collector was prepared in anhydrous alcohols at the concentration of $10^{-2}$ mol/dm$^3$. The experiment was started by introducing 4 cm$^3$ of this solution into 186 cm$^3$ aqueous solution of the colligend ions in a flotation column; hence, the initial concentration of the collector in the flotation medium was $2 \times 10^{-4}$ mol/dm$^3$ at an alcohol concentration of 2%. It should be additionally clarified that after introducing the collector into the solution containing $Me^{2+}$ and $SCN^-$, precipitation of the quaternary ammonium metal thiocyanate salt followed. 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) at the base. Nitrogen was passed at a flow rate of 30 cm$^3$/min for 10 min. The effectiveness of foam separation was calculated on the basis of determining the metal in the initial suspension and in the residual bulk suspension. The determinations were preceded by decomposition of the metal and collector compound. For this purpose a sample of residual 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 the metals were determined by the spectrophotometric method; cobalt with Nitroso R-salt (*12*) and cadmium with dithizone (*12, 13*). The cetyltrimethylammonium collector was determined by the spectrophotometric method with Orange II (*14*).

Measurements of the foaming properties of the flotation suspension were carried out by the Sun (*15*) method by using a column for foam separation.

The surface tension ($\sigma$) of the suspension was measured with a Du Nouy tensiometer, the ring of which was made from platinum wire.

The volume of the liquid removed with the bubbles was determined by using the monobubble apparatus described elsewhere (*16*). The change in the volume of the liquid removed from suspensions of various concentrations of thiocyanate and in the presence and absence of cobalt was determined in relation to the time of gas flow. The kinetic curves of liquid removal were then plotted. From these curves the volumes of the liquid removed after 5 min from the beginning of the process were read.

Electric surface potential (adsorption potential $\Delta V$) was measured using the ionization method with Am as the source of α-particles (*17, 18*). The activity of the source was 30 μCi. Measurements were carried out on a stationary suspension surface 10 min after its formation. The potential value was measured in the following systems: (a) calomel electrode/"basic" solution of $Me^{2+}$-air/Au and (b) calomel electrode/flotation suspension-air/Au. The electric surface potential $\Delta V$ is then the difference between the potential of the flotation suspension and the potential of the "basic" solution at $10^{-4}$ mol/$dm^3$ concentration of cadmium sulfate or cobalt chloride.

## RESULTS

The effect of thiocyanate concentration on cobalt removal in the presence of 2% of each of the various alcohols is presented in Fig. 1(A), and the change of cobalt complexation in relation to thiocyanate concentration (taken from the literature (*19, 20*)) in Fig. 1(B). The alcohol concentration mentioned above was obtained by introducing an alcohol solution of the collector into the aqueous colligend solution. The initial collector concentration (cetyltrimethylammonium bromide) in the flotation medium was $2 \times 10^{-4}$ mol/$dm^3$ and the cobalt concentration was $10^{-4}$ mol/$dm^3$. In analyzing the results of foam separation it should be remembered that alcohols with one to three carbon atoms dissolve completely in water, whereas 1-butanol dissolves only to 9% (and its solubility decreases in the presence of thiocyanate). During introduction of butanol collector solution into the aqueous colligend solution in a flotation column, droplets of the former rose, preventing the distribution of collector in the bulk aqueous solution. This had a negative effect on cobalt removal (Curve 4 is the lowest in Fig. 1A). From Fig. 1(A) it can be seen that metal removal increases with increasing thiocyanate concentration (to about 0.5 mol/$dm^3$), and this behavior is similar to that of the anionic cobalt complex $(Co(SCN)_4)^{2-}$ in Fig. 1(B). In addition, metal removal in the presence of alcohols decreases in the sequence butanol < methanol < ethanol < propanol. Alcohols produced an improvement in cobalt removal kinetics in the same sequence (*21*).

Figure 2 shows the effect of thiocyanate concentration on the foaming of the flotation medium in the presence of methanol (2%). An increase in thiocyanate concentration decreases the time for maximum foam formation and decreases the foam height. Based on observations of the foam separation process and changes of $\sigma$ or $\Delta V$ of the suspension in the presence of various alcohols (Figs. 4 and 5), it can be stated that foaming of suspensions increases with an increase in the number of carbon atoms in the alcohol chain. A similar conclusion can be drawn from literature data; for improvement of solution foaming properties in ore flotation processes, small amounts of alcohols are sometimes added (*22*).

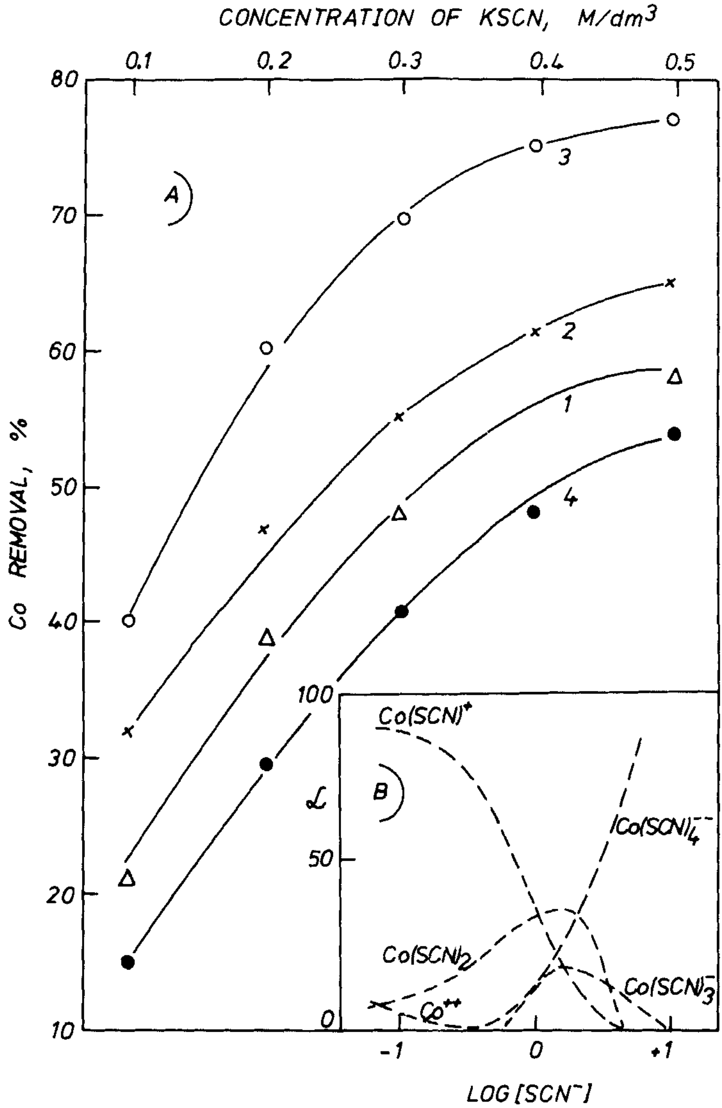


FIG. 1. (A) Influence of thiocyanate concentration on cobalt removal in the presence of different alcohols in solution: (1) methanol, (2) ethanol, (3) propanol, and (4) butanol. (B) Correlation between cobalt complexation and concentration of thiocyanate ligands (*19*, *20*).

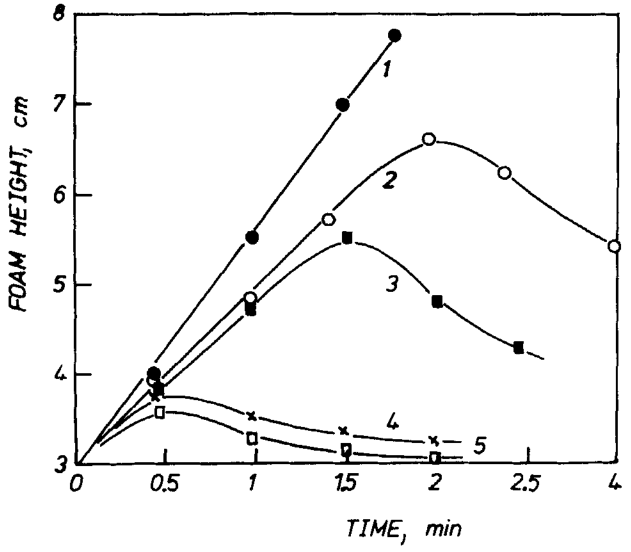


FIG. 2. The effect of increasing additions of thiocyanate on foam stability: without salt (1), and in the presence of thiocyanate (0.025 *M* (2), 0.05 *M* (3), 0.1 *M* (4), and 0.2 *M* (5).)

Figure 3 illustrates the effect of thiocyanate concentration on liquid removal with gas bubbles from suspensions used for flotation (Curve 1) and from suspensions not containing a metal (Curve 2). With increasing thiocyanate concentration, hydration of bubbles decreases, and it is much lower in the presence of a metal in suspension. The studies of Skrylev et al. (*6*) show that foam hydration increases with increasing alcohol molecule size.

The changes of the surface properties of cobalt or cadmium containing flotation suspensions with changing thiocyanate and alcohol concentrations are presented in Figs. 4 and 5. As can be seen, $\sigma$ and $\Delta V$ of the suspensions increase with an incresae of the thiocyanate concentration in the series butanol < propanol < ethanol < methanol < without alcohol and collector. Moreover, the values of these parameters are higher in the presence of cadmium (Curves 1–4) than of cobalt (Curves 5–8). Values of the surface tension and the surface potentials of these suspensions have been given for the range of thiocyanate concentrations in which metals were floated. Foam separation of cadmium under these conditions was described elsewhere (*8*). From a comparison of Figs. 4 and 5 with Fig. 1, together with the literature data for cadmium (*8*), it appears that the change of these parameters is similar to that of the degree of metal

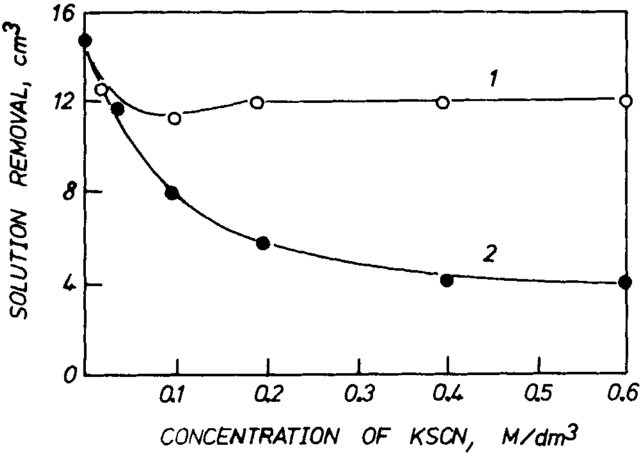


FIG. 3. Influence of thiocyanate concentration on solution removal with bubbles: (1) without metal, and (2) in the presence of cobalt.

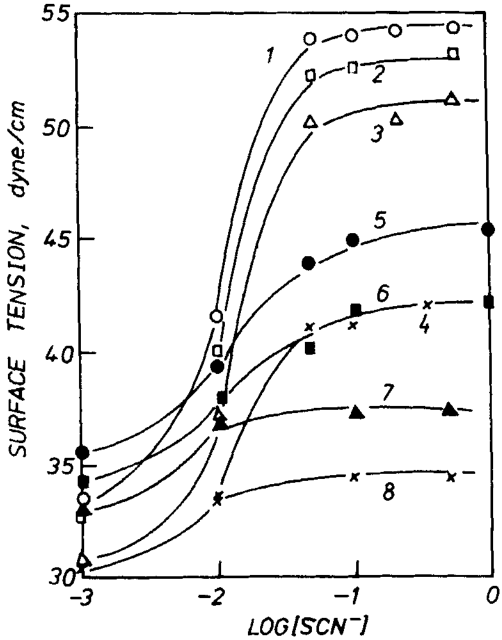


FIG. 4. Changes of surface tension of different alcohol solutions in relation to thiocyanate concentration (1-4 for cadmium, 5-8 for cobalt): (1 and 5) methanol, (2 and 6) ethanol, (3 and 7) propanol, and (4 and 8) butanol.

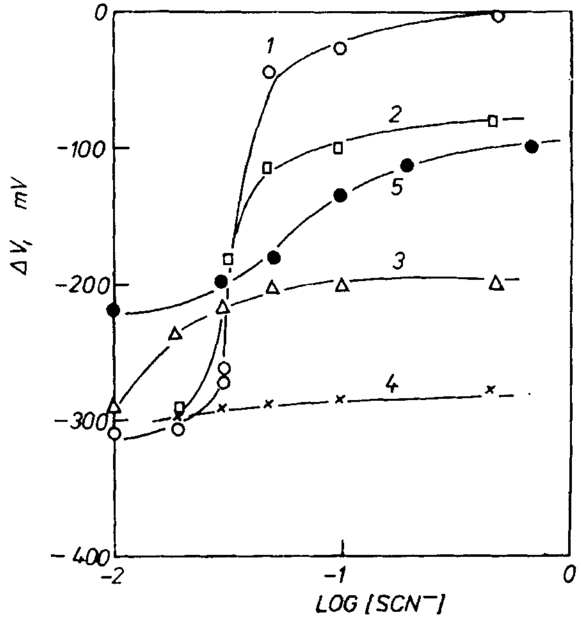


FIG. 5. Changes of adsorption potential of different alcohol solutions in relation to thiocyanate concentration. Curves keyed as in Fig. 4.

complexation produced by the change in thiocyanate concentration. At the thiocyanate concentration for which metal removal is the highest, both the surface tension and the adsorption potential are also the highest.

The effect of alcohol concentration on cobalt removal from suspensions at 0.2 mol/dm$^3$ thiocyanate, when cobalt anions are present (compare Fig. 1B), is presented in Fig. 6. From Fig. 6 it can be seen that the removal curves have maxima at different alcohol concentrations; at about 10% propanol, 14% ethanol, and 17% methanol. Maximum removal increases with alcohol concentration, the shorter the hydrocarbon chain of the alcohol. It is therefore postulated that foam becomes less stable at relatively high alcohol concentrations.

Figure 7 illustrates the effect of alcohol concentration on (a) collector removal (Curves 1–3 for methanol, ethanol, and propanol, respectively); (b) concentration of the collector remaining in solution after sublate precipitation but before flotation (Curves 4–6 correspond to alcohols in the above sequence); and (c) concentration of cobalt remaining in solution after sublate precipitation (Curves 7–9 plotted in the above

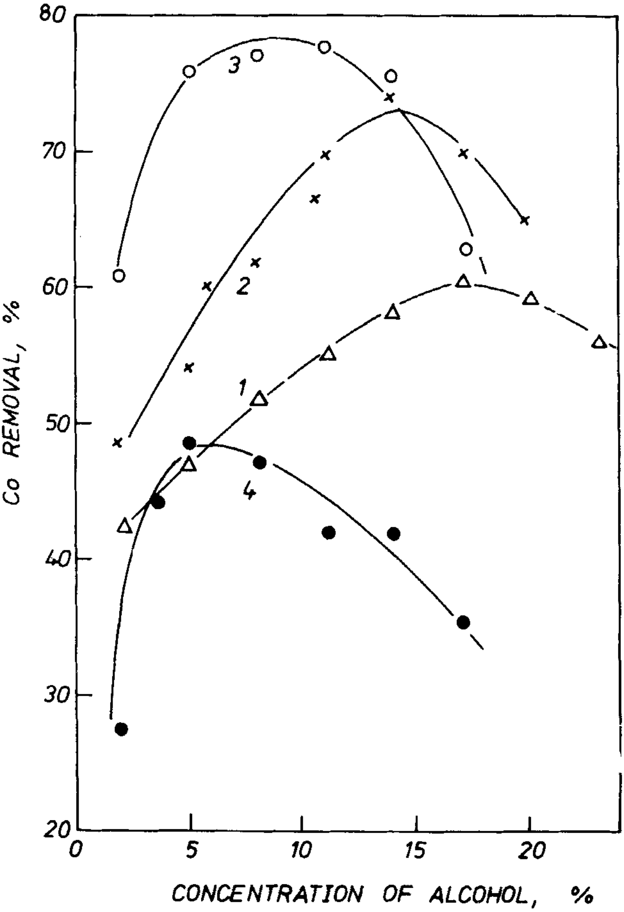


FIG. 6. Effect of alcohol concentration on cobalt removal from thiocyanate solutions. The curves for individual alcohols are keyed as in Fig. 1(A).

sequence of alcohols) but before flotation. The initial concentration of thiocyanate was 0.2 mol/dm$^3$, cobalt was $10^{-4}$ mol/dm$^3$, and the collector was $2 \times 10^{-4}$ mol/dm$^3$. From Fig. 7 it appears that collector removal decreases with increasing alcohol concentration. A distinct removal decrease is seen at higher and higher alcohol concentrations the shorter its hydrocarbon chain. By analyzing Curves 4-6, it is seen that at the lowest alcohol concentration (2%) the collector is almost completely precipitated (its lowest concentration in solution). At higher alcohol

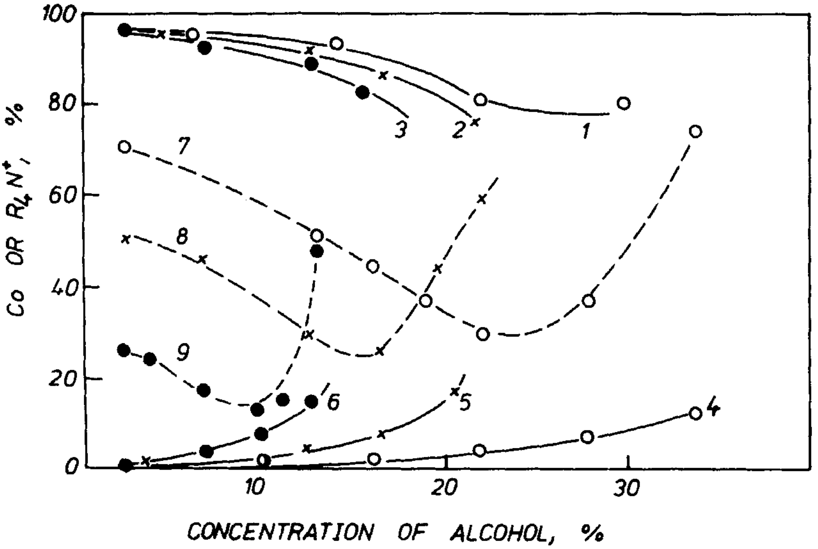


FIG. 7. Influence of alcohol concentration and the number of carbon atoms of alcohol molecules on collector removal (Curves 1-3), on the amount of collector in solution (Curves 4-6), and on the amount of cobalt in solution (Curves 7-9). Curves 1, 4, and 7 are for methanol; Curves 2, 5, and 8 are for ethanol; and Curves 3, 6, and 9 are for propanol.

concentrations the collector concentration in the solution increases. Dissolution of the collector sediment occurs at lower alcohol concentrations, the longer its hydrocarbon chain.

From Curves 7-9 it can be seen that with an increase of alcohol concentration the cobalt concentration in the solution first decreases (the amount of sublate increases) and then begins to increase (sublate dissolution starts). A minimum cobalt concentration in the solution (maximum precipitation) occurs at higher and higher alcohol concentrations, the shorter its hydrocarbon chain. Comparison of Curves 7-9 with Curves 4-6 shows that cobalt precipitation in the form of sublate is lower than precipitation of the collector, although a stoichiometric collector/cobalt ratio of 2:1 was used.

Curve 1 in Fig. 8 illustrates the effect of the composition of an alcohol mixture (propanol with methanol) in water on cobalt removal. The concentration of the alcohol mixture in water was 15% v/v, while the ratio of propanol to methanol was varied. The other flotation conditions were the same as those shown in Fig. 6. From Curve 1 it is seen that maximum cobalt removal occurs near a propanol:methanol concentration ratio of 7.5:7.5.

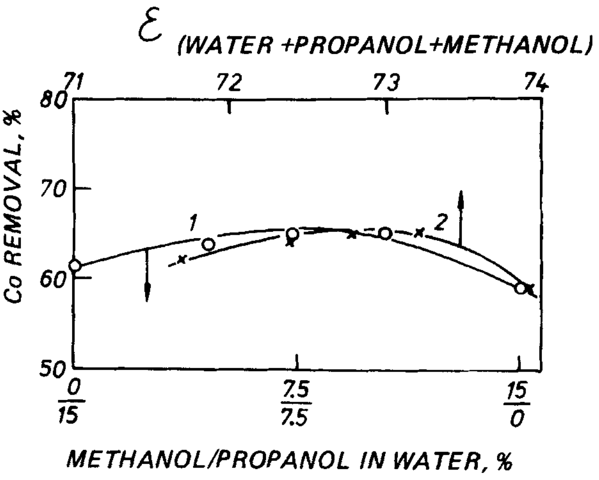


FIG. 8. Effect of the propanol/methanol concentration ratio in water on cobalt removal (1), and correlation between the removal of cobalt and the dielectric constant of water + propanol + methanol solutions (2).

Figure 9 shows the effect of propanol concentration of the removal of cadmium and collector (Curves 1 and 3) and on sublate solubility (Curve 2 expresses cadmium concentration in the solution, whereas Curve 4 expresses collector concentration) before flotation. The other flotation conditions were the same as those given in Figs. 6 and 7. From Curves 1 and 2 it is seen that maximum removal occurs at about 10% concentration of propanol in the solution, while cadmium concentration in the solution is then the lowest. However, the lowest collector concentration in the solution occurs at 2% propanol and increases with increasing propanol concentration. The decrease in the amount of the collector in the sediment is similar to the removal decrease with increasing propanol concentration. However, the values of these parameters are not identical because removal is lower than precipitation of the collector.

Figure 10 represents cobalt removal as a function of the dielectric constant of water–alcohol solutions ($\varepsilon_{(\text{water+alcohol})}$). The dielectric constant was calculated according to a formula given in the literature (*23*):

$$\varepsilon_{(\text{water+alcohol})} = \frac{V}{100}\varepsilon_{\text{alcohol}} + \frac{100 - V}{100}\varepsilon_{\text{water}}$$

where $V$ and $\varepsilon_{\text{alcohol}}$ are the v/v percentage and dielectric constant of

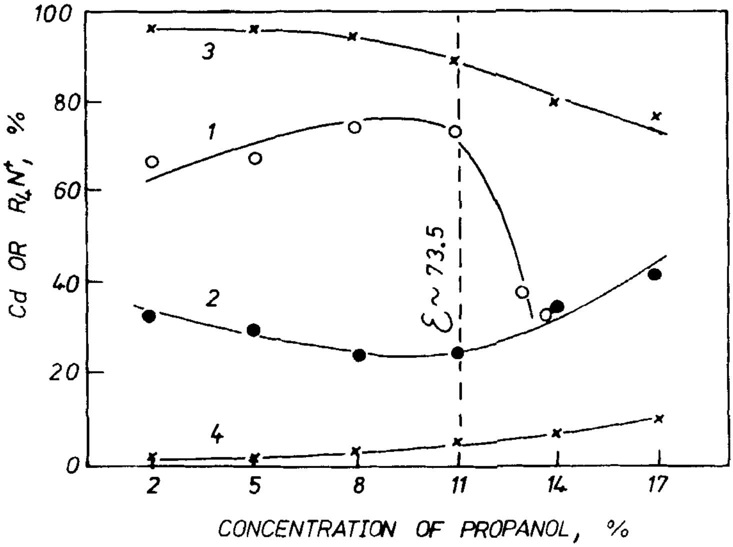


FIG. 9. Influence of propanol concentration on cadmium removal (1), on the amount of cadmium in solution (2), and on collector removal and the amount of collector in solution (3 and 4).

alcohol, and (100 − $V$) and $\varepsilon_{\text{water}}$ are the v/v percentage and dielectric constant of the water. The following ε values of pure components were taken from the literature (*24*): for water, 81; for methanol, 33.63; for ethanol, 24.3; for propanol, 21.8; and for butanol, 17.8. The characteristic feature of Curves 1–3 in Fig. 10 is the occurrence of maximum cobalt removal at a dielectric constant value close to 73.5. This does not apply to Curve 4 (for butanol) because of the lower solubility of this alcohol in water as mentioned earlier. A similar correlation of cobalt removal with the dielectric constant of a ternary solution (water + propanol + methanol) is shown by Curve 2 in Fig. 8. ε values of ternary mixtures of the same composition as for Curve 1 are given on the axis. To calculate ε of the solutions, the mixture of propanol and methanol was taken as one component with water as the other. From Fig. 10 it can be seen that maximum removal for such solutions occurs near a dielectric constant of 73.5. By analyzing the course of cadmium removal as a function of propanol concentration (Fig. 9), maximum cadmium removal may be expected to be obtained from the medium with this dielectric constant.

Figure 11 illustrates the effect of alcohol concentration on the surface tension of the suspensions (Fig. A) and on the adsorption potential of

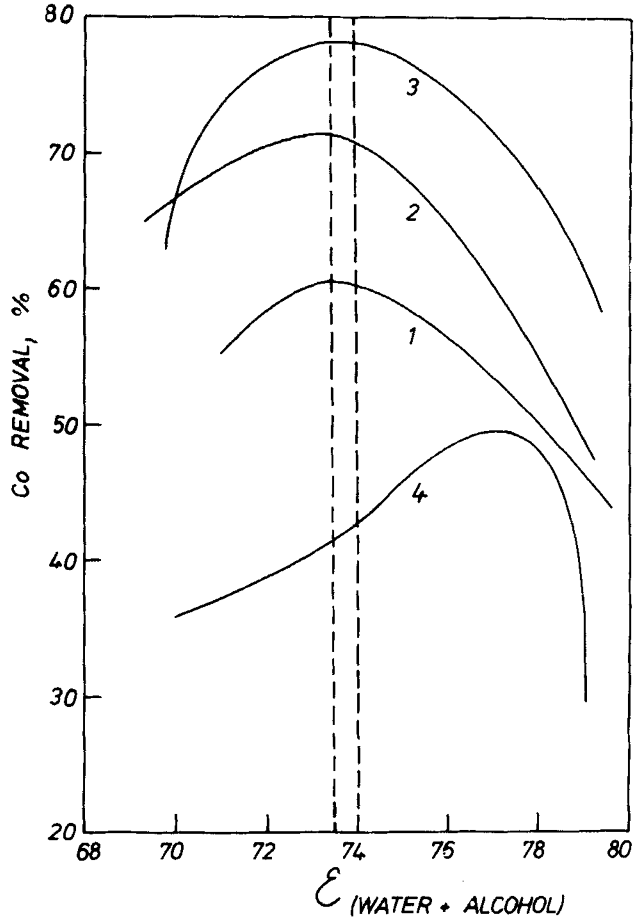


FIG. 10. Correlation between the removal of cobalt and the dielectric constant of water-alcohol solutions. Alcohols are keyed as in Fig. 1(A).

suspensions (Fig. B) in the presence of cadmium (Curves 1–4) and cobalt (Curves 5–8). The initial concentrations of the components were $10^{-4}$ mol/dm$^3$ of cadmium or cobalt, $2 \times 10^{-4}$ mol/dm$^3$ of the collector, and 0.2 mol/dm$^3$ of the thiocyanate. From Fig. 11 it is seen that both the surface tension and the surface potential of the suspension continuously decrease with increasing alcohol concentration and the number of carbon atoms in the alcohol. The change of these parameters was

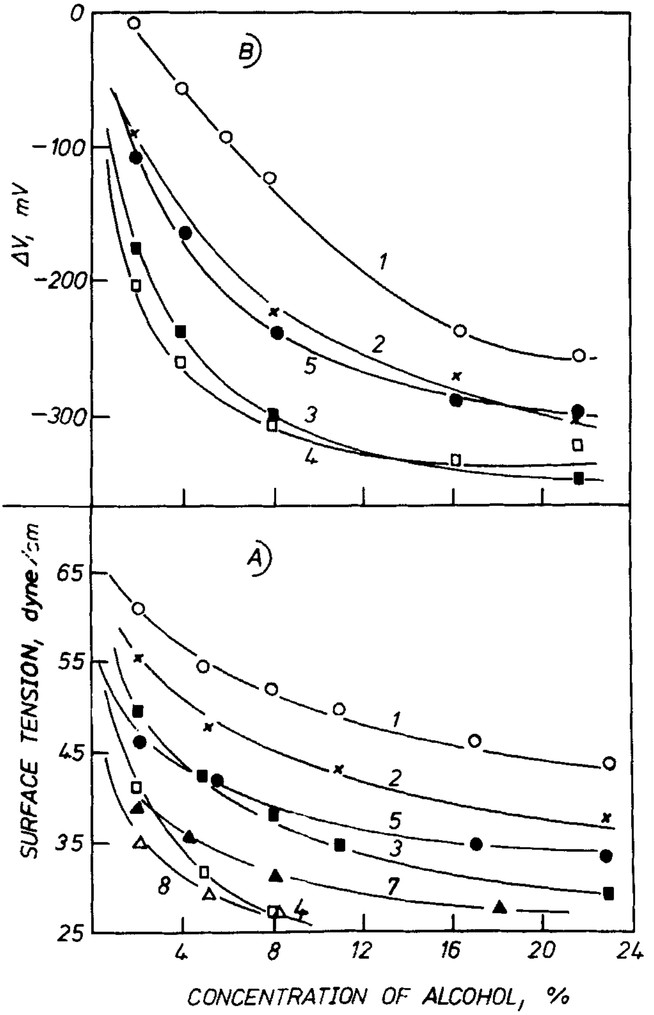


FIG. 11. Changes of surface properties of different alcohol solutions in relation to their concentrations. (A) Surface tension; (B) adsorption potential. Curves 1-4 are for cadmium; Curves 5-8 are for cobalt. Individual alcohols are keyed as in Fig. 4.

determined only up to 9% butanol in the medium. The values of $\sigma$ and $\Delta V$ for cobalt-containing suspensions are smaller than in the presence of cadmium. This sequence is compatible with the direction of the stability increases of anion complexes of the two metals (*8, 19, 20*).

## DISCUSSION

It can be seen from Fig. 1(A) that the removal of cobalt in the foam separation process increases with an increase in the concentration of thiocyanate in solution. If we assume the least complicated mechanism of collector $C_{16}H_{33}N^+(CH_3)_3$ interaction with the cobalt ion, i.e., electrostatic, it can be concluded that the cobalt removed is present as a complex anion. The course of cobalt removal and metal complexation vs thiocyanate concentration (Figs 1A and 1B) indicates that the metal is best removed in the form of $(Co(SCN)_4)^{2-}$.

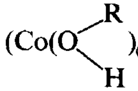
The collector–colligend product is removed as a blue scum, and the foam produced is lower (Fig. 2) and relatively drier (Fig. 3) as the concentration of thiocyanate increases. Consequently, a very high concentration of cobalt is found in the foam. The relationship between removal and metal complexation by thiocyanate and iodide, published by Jurkiewicz and Waksmundzki (*8, 9*), and the results of metal foam fractionation from chloride and cyanide solutions, published by Walkowiak et al. (*10, 11*), have been confirmed.

A thiocyanate concentration increase causes an increase in the surface properties of the suspension, which can be seen from Figs. 4 and 5. The suspension has the highest surface tension and adsorption potential at the highest thiocyanate concentration, where complexation of the metal and metal removal are the highest. It appears that binding of the collector by complex anions of the metal (it can also combine with thiocyanate anions, as a result of exchange of counterions $Br^-$ for $SCN^-$, as shown by Grieves et al. (*25, 26*) and Charewicz and Strzelbicki (*27*)) causes the collector concentration to decrease in solution and at the solution/gas interface. This causes a decrease in the height and hydration of foam with increasing complexation of the metal (Figs. 1B, 2, and 3). From these facts it may be postulated that the quaternary ammonium salt particles stabilize gas bubbles in the foam. As the ability of thiocyanates to complex cadmium is greater than that to complex cobalt (*8, 19, 20*), the collector concentration is lower in the solution after cadmium sublate precipitation than after cobalt sublate precipitation, hence the values of $\sigma$ and $\Delta V$ for suspensions are higher in the presence of cadmium than of cobalt. A similar increase of the surface properties of suspensions with increased complexation of the metal by thiocyanate and iodide was found earlier (*8, 28*). Moreover, Okamoto and Chou (*29–31*) reported similar relationships between the formation constants and surface tension of solutions of metals-4-dodecyldiethylenetriamine complexes.

Taking into consideration the influence of alcohol on removal, attention should be drawn to its possible effect on two principal stages of foam separation: (a) metal complexation and formation of sublates and (b) change of the solution/gas interface structure. The formation of complexes in aqueous-alcohol solutions is easier than in aqueous solutions, and it increases with an increase of the alcohol concentration and the number of carbon atoms in the alcohol.

The presence of alcohol in the solution is a dehydrating factor (*23, 32*). Alcohols belong to the so-called oxo solvents which possess an oxygen atom with a pair of electrons which are able to form a donor-acceptor bond with metal cations and water molecules. For this reason alcohol molecules can effectively compete with water molecules in metal cations solvation, and they facilitate water replacement from the inner zone of the aquo-complex for thiocyanate ligands and cause the equilibrium to shift to the right (*33, 34*):

$$(\mathrm{Co(OH_2)_6})^{2+} + n\mathrm{X}^- \rightleftarrows (\mathrm{Co(OH_2)}_{(6-n)}\mathrm{X}_n)^{(2-n)} + n\mathrm{H_2O}$$

to the complex $(\mathrm{Co(OH_2)_2X_4})^{2-}$ which is in equilibrium with $(\mathrm{CoX_4})^{2-}$ + $2\mathrm{H_2O}$, in which $\mathrm{X}^-$ = ligand ($\mathrm{SCN}^-$, $\mathrm{I}^-$, $\mathrm{Br}^-$, or $\mathrm{Cl}^-$). In an analogous way the solvated complex can be written as  $(\mathrm{Co(O}\genfrac{}{}{0pt}{}{\mathrm{R}}{\mathrm{H}})_{(6-n)}\mathrm{X}_n)^{(2-n)}$. At a low concentration of alcohol, mixed solvates with water can be formed. When the hydration of metal complexes decreases, then the complex forms a sublate with the collector more readily. Aqueous-solvate and solvate complexes of metal-thiocyanate solvated by different alcohols possess different hydrophobicities, and thus they show different affinities to the collector. This is proved by Curves 7–9 in Fig. 7 and Curves 2 in Fig. 9, from which it appears that metal concentration in the solution decreases (the amount of sublate increases) with an increase of alcohol concentration within a certain range and with an increase in alcohol size. These conditions positively affect the foam separation of metals (Figs. 1, 6, and 9, Curve 1).

The presence of alcohol decreases the dielectric constant of the solution the longer the alcohol hydrocarbon chain and with increasing alcohol concentration, deepening the blue coloring of cobalt sublate suspension. According to Babko (*23*) and Morrison and Freiser (*32*), there should be a simple relationship between p*K* of the complex (dissociation constant) and ε of the solvent (dielectric constant). Hence it appears that with an increase of alcohol concentration and the size of the alcohol molecule, dehydration of metal complexes and the collector and their stability should increase. Similarly, the amount of metal in the form of sublate sediment should increase continuously. However, as seen from Figs. 6, 7, and 9, the curves illustrating the amount of metal in the sublate sediment and the removal curves show maxima as a function of alcohol concentration. Maximum values of the curves appear at lower and lower alcohol concentrations the longer the hydrocarbon chain.

An important parameter which affects the stability of sublates is the dielectric constant of the medium. Cobalt removal as a function of the dielectric constant of water–alcohol solutions is presented in Figs. 8 and 10. It is seen that maximum metal removal occurs at an equal value of the dielectric constant of solutions of various alcohols, close to 73.5. Because of different values of the dielectric constants of pure alcohols (*24*), the above value of $\varepsilon_{(\text{water+alcohol})}$ is obtained at concentrations of about 17% methanol, 14% ethanol, and 10% propanol (butanol has been excluded from the discussion because of its very limited solubility in water). From a comparison of Figs. 6, 7, and 9 with Fig. 10, it appears that near a dielectric constant of 73.5 there is also a minimum of metal concentration in solution. This fact may be explained as follows. Alcohol molecules can effectively compete with water molecules in sublate (complexes) solvation and, if solvation is strong enough (in a solution of appropriate alcohol concentration for an appropriate hydrophilic–lipophilic balance, HLB, of the alcohol molecule) hydrophobic sublates dissolve. This problem has been partially studied for extraction processes and chromatography of metal complexes (*19, 20, 33–35*). It appears from Fig. 7 (Curves 7–9) and from Fig. 9 (Curve 2) that the activity of alcohols as sublate solvents is higher the longer the alcohol hydrocarbon chain, which is in accordance with the decreasing HLB of alcohols (*36, 37*). From the above considerations it can be seen that in a medium with a dielectric constant lower than 73.5, transformation of the sublate sediment quaternary ammonium metal thiocyanate salt into a soluble form, which may be a solvated ionic pair, $[(\text{Me(SCN)}_4)^{2-}, 2\text{R}_4\text{N}^+ \cdot n\text{Solvent}]$, takes place.

From the figures it also appears that at 2% alcohol concentration (and at 0.2 mol/dm$^3$ thiocyanate), collector precipitation is almost complete, whereas metal precipitation in the form of the sublate is only partial and increases the longer the alcohol hydrocarbon chain (the smaller the value of alcohol HLB). Taking into consideration this and the fact that the initial collector concentration was stoichiometric to that of the metal, it should be assumed that under conditions where $[\text{SCN}^-] \gg [\text{Me}^{2+}] +$

$[R_4N^+]$, collector precipitation occurs not only in the form of a sublate with a complex metal anion but also with thiocyanate anion in the form of the quaternary salt of cetyltrimethylammonium thiocyanate, which is in agreement with the affinity series of inorganic anions to alkylammonium cations ($SCN^- > Br^-$) of Grieves et al. (*25, 26*) and Charewicz and Strzelbicki (*27*), as well as with previous studies of foam separation (*8*). Dissolution of cetyltrimethylammonium thiocyanate sediment by alcohol may also be treated as a transformation of the sediment into a soluble form which may be a solvated ionic pair [$SCN^-$, $R_4N^+ \cdot n$ Solvent].

The soluble ion pairs are also foam separated, and then we observed both ion flotation of the insoluble sublate and foam fractionation of the soluble species. In all precipitation and foam separation experiments (Figs. 6, 7, and 9), metal removal increases with an increasing amount of sublate in flotation suspension. This problem, i.e., the effect of the amount of the surfactant–colligend precipitate and particle size on the extent of ion flotation, was studied by Grieves et al. (*2*). They indicated that the effectiveness of the alkylammonium surfactant as a precipitant and collector increased with increasing chain length from $C_{10}$ to $C_{16}$ (a surfactant with a chain length of $C_{18}$ is a good precipitant but a bad collector).

By comparing collector removal with its precipitation (Curves 1–3 with Curves 4–6 in Fig. 7 and Curves 3 and 4 in Fig. 9) and comparing cadmium removal with its precipitation (Curves 1 and 2 in Fig. 9), it is found that collector removal and cadmium removal are lower than their precipitation. The change of $\sigma$ and $\Delta V$ of the suspensions (Figs. 4, 5, and 11) and the above facts imply that alcohol molecules compete with the collector–colligend compounds for adsorption on the gas bubble. Because the quaternary ammonium salt particles stabilize gas bubbles, and at a higher alcohol concentrations the amount of salt particles decreases, the foam becomes less stable.

The competitive adsorption of alcohol is more effective the longer the alcohol hydrocarbon chain (and the more surface-active the alcohol, in accordance with Traube's principle) and the higher is the alcohol concentration. These conclusions are supported by the studies of Skrylev et al. (*6*) and Rodakiewicz (*38*), who state that adsorption of an alkylammonium surfactant at the solution/gas interface decreases with the addition of alcohol to the solution, and the rate of alkylammonium surfactant exchange with the alcohol largely depends on the concentration and surface activity of the alcohol. The competition of alcohol adsorption with sublate is an additional reason (besides sublate solubility) for a metal removal decrease at high alcohol concentrations in the flotation medium.

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