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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
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To cite this Article Jurkiewicz, Kazimierz(1987) 'Ion Flotation and Solvent Extraction of Ferric Thiocyanate Complexes', Separation Science and Technology, 22: 12, 2381 — 2402
To link to this Article: DOI: 10.1080/01496398708057193
URL: http://dx.doi.org/10.1080/01496398708057193

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SEPARATION SCIENCE AND TECHNOLOGY, 22(12), pp. 2381-2402, 1987

Ion Flotation and Solvent Extraction of Ferric Thiocyanate Complexes

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Abstract

The influence of thiocyanate and accompanying mineral acids concentration on the effectiveness of Fe(III) ion flotation, Fe(III) precipitation in cetyltrimethylammonium ferric-thiocyanate form (as sublate), and Fe(III) extraction using ethyl acetate was studied. The effectiveness of these processes improves with the extent of Fe(III) complexation by thiocyanates. In the presence of acids, flotation and precipitation are increased as follows: $HClO_4 < HCl < HNO_3 < H_2SO_4$. The position of H_3PO_4 in this series changes with changing thiocyanate concentration. Extraction effectiveness is increased in the series: $H_3PO_4 < H_2SO_4 < HNO_3$, $HClO_4$, HCl. The following points are discussed: (a) the influence of acid anions competing with thiocyanate anions in Fe(III) complexation; (b) the influence of the competition between acid anions and complex ferric-thiocyanate anions in sublate formation; (c) the influence of hydrogen ion concentration increase in thiocyanate medium on the results of Fe(III) flotation, precipitation, and extraction; and (d) the influence of anion affinity for a collector on the solution surface properties and on Fe(III) flotation.

INTRODUCTION

Wastewater treatment and progress in the analytical chemistry of trace metals depend on the development of suitable trace metal separation and concentration methods. Because of the great volume, extent of dilution, and variety of wastewaters, such physicochemical methods as solvent extraction, ion exchange, chromatography, and foam separation techniques [the classification of these last has been proposed by Karger et al.

(*1*)], are of great importance. In these separation methods, surface-active agents are employed: liquid ion exchangers are used in extraction and chromatography, and collectors are employed in foam separation. Their relevant characteristics are dissociation and the exchange of counterions of long-chain ions for other counterions from aqueous solution (i.e., the formation of surfactant–colligend compounds) as well as their ability to form foams on the surface of the aqueous solution.

Many successful applications of the foam separation process have been reported by Sebba (*2*), Rubin (*3*), Kuzkin and Golman (*4*), Lemlich (*5*), Grieves (*6*), and Grieves and Charewicz (*7*). A review of recent investigations was published by Clarke and Wilson (*8*).

Sebba (*2*) reports that "Iron is not the sort of element which is likely to be concentrated by ion flotation for its value. Nevertheless, as it is an element commonly found in industrial or mining solutions, it is a contaminant of more valuable elements. Its removal very often considerably improves the value of the associated element, and such removal is not always easy." For this reason the possibility of Fe(III) removal by foam separation methods should be studied.

Foam separation of iron as (a) $Fe(CN)_6^{4-}$ and $Fe(CN)_5H_2O^{3-}$, (b) $FeFe(CN)_6^{-}$ and $FeFe(CN)_6^{2-}$ and (c) $Fe(II)[Fe(CN)_6Fe]$ and $Fe(II)[Fe(CN)_6Fe]_2$ was examined by Grieves and Bhattacharyya (*9*, *10*). Foam separation of the first species is ion flotation, foam separation of the second (of Prussian Blue with the complexed cyanide) is colloid flotation, and foam separation of the third is precipitate flotation. Foam separation of iron cyanide complexes was also reported by Skrylev and Mokrushin (*11*), Skrylev and Trigubienko (*12*), Amanov (*13*), Skrylev and Amanov (*14*), and Sviridov (*15*). The effect of pH on Fe(III) flotation was examined by Rubin and Johnson (*16*). The macromolecular flotation of Fe(III) by the combined use of charcoal and hexadecyltrimethylammonium chloride was studied by Sasaki et al. (*17*). Elhanon and Karger (*18*) reported the results of solvent sublation of Fe(III) ions from aqueous hydrochloric acid solutions. Solvent sublation of Fe(III) was also reported by Bittner et al. (*19*). A series of investigations has been conducted on the adsorbing colloid flotation of metal ions by FeS and $Fe(OH)_3$. Kim and Zeitlin (*20–22*) studied adsorbing colloid flotation of copper, molybdenum (as MoO_4^{2-}), uranium (as $UO_2(CO_3)_3^{4-}$), phosphate, and arsenate from seawater using ferric hydroxide and sodium lauryl sulfate. Clarke et al. (*23*) studied adsorbing colloid flotation, using ferric hydroxide to remove complexed cyanides. Wilson et al. (*24–29*) used FeS and $Fe(OH)_3$ to remove lead, cadmium, and copper from industrial waste samples by adsorbing colloid flotation. Recently, Walkowiak (*30*) reported the result of foam fractionation for several metal cations together with Fe^{3+} using anionic collectors.

Among the studies published on the foam separation of Fe(III), very few fundamental papers have been devoted to foam separation of anionic complexes. Up to now, ion flotation of ferric thiocyanate anionic complexes has not been reported, although these complexes have attracted interest in their use in extraction and chromatography (*31–36*) and for preliminary concentration of trace amounts of iron in analytical chemistry (*37–41*).

The present work has therefore been undertaken to obtain further information on the ion flotation of ferric thiocyanate anionic complexes and on the solvent extraction of these complexes under flotation conditions to make a comparison between adsorptive bubble separation and solvent extraction processes [papers comparing these two methods are also few in number; e.g., Elhanon and Karger (*18*), Charewicz et al. (*42*), Charewicz (*43*), and James and Robinson (*44*)].

EXPERIMENTAL

Initially a stock solution of Fe(III) was prepared at the concentration of 10^{-2} *M*/dm^3 by dissolving $FeNH_4(SO_4)_2 \cdot 12H_2O$ (analytically pure, produced by POCH-Gliwice, Poland) in double distilled water with the addition of concentrated H_2SO_4 (in the proportion 1 dm^3 of solution and 5 cm^3 of concentrated acid). Next, feed solutions at a Fe(III) concentration of 10^{-4} *M*/dm^3 were obtained by diluting the stock solution with aqueous thiocyanate solution. The pH of these solutions was ~3.5 and they were used in the experiments.

The other reagents, potassium salts (thiocyanate, chloride), ammonium perchlorate, acids (hydrochloric, perchloric, nitric, sulfuric, phosphoric), and the organic solvent, ethyl acetate, were also analytically pure, from POCH-Gliwice, Poland.

Analytically pure cetyltrimethylammonium bromide, used as a collector, was produced by Chemapol, Prague. The collector was dissolved in methanol at a concentration of 10^{-2} *M*/dm^3. The foam separation process was started by introducing 2 cm^3 of this solution into 98 cm^3 aqueous solutions of the colligend (ferric–thiocyanate flotable species) in a flotation column while gas was passing through the aqueous solution. The collector concentration in the feed solution was 2×10^{-4} *M*/dm^3 [i.e., below the critical micelle concentration in aqeuous solution (*43*)] at an alcohol concentration of 2%. After introduction of the collector into the solution containing Fe(III) and KSCN (NH_4SCN was used in the presence of $HClO_4$), precipitation of cetyltrimethylammonium salt followed. In the presence of HCl a few drops of hydrogen peroxide solution were added to the suspensions.

Foam separation was carried out in a multibubble column which was 25 cm high and 100 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 20 cm^3/min for 7 min. The effectiveness of foam separation was calculated on the basis of the determinations of iron in the feed and residual suspensions. The determinations were carried out by the thiocyanate method (*37–39*). The red complex Fe(III)-thiocyanate was quantitatively extracted from a 10 cm^3 portion of the aqueous solution by two 5 cm^3 portions of ethyl acetate. The absorbance of the organic phase at 495 nm was then measured with a Spekol (C. Zeiss) spectrophotometer.

The surface tension of the suspension was measured with a Du Noüy tensiometer with a platinum wire ring.

Electric surface potential (adsorption potential, ΔV) was measured using the ionization method with Am (activity 30 μCi) as a source of α-particles (*45*, *46*). The potential value was measured in the following systems: (a) calomel electrode/"basic" solution–air/Au and (b) calomel electrode/suspension of collector and thiocyanate–air/Au or calomel electrode/suspension of collector, thiocyanate, and iron–air/Au. The electric surface potential ΔV is then the difference between the potential of the suspension and the potential of the "basic" solution which was thiocyanate solution at 10^{-4} M/dm^3 concentration or Fe(III) solution at 10^{-4} M/dm^3 concentration.

Measurements of the foaming properties of the suspension were carried out by the pneumatic method (*47*) in which nitrogen is injected into the suspension through sintered glass spargers (using the column for foam separation). The foam heigh is measured while the gas continues to produce bubbles.

Solvent extraction was carried out by shaking together 10 cm^3 of aqueous suspension of the collector, iron, and thiocyanate (and acids) with two 5 cm^3 portions of ethyl acetate. Shaking was continued for 15 min, and ~30 min were allowed for separation of the phases. After the experiment, the iron concentration in the aqueous phase was determined as above (iron concentration was also determined from the color of the organic phase). The removal of Fe(III) by foam separation, as well as by solvent extraction, was evaluated from the relationship $R = (1 - C_r/C_i) \times 100$, where C_r and C_i are the concentrations of iron in the residual suspension (after flotation or extraction) and in initial (feed) suspension, respectively.

RESULTS

After the introduction of cetyltrimethylammonium bromide (the collector) into the solution containing Fe(III)-SCN^- complex (the colligend), precipitation of the quaternary ammonium salt followed (the sublate). Thus this foam separation technique is ion flotation (*1–6*).

In the first series of experiments the extent of ion flotation of Fe(III) and its precipitation (as sublate) were studied. The effect of thiocyanate concentration (over a range of $[SCN^-]/[Fe^{3+}]$ ratios from ~500 to 4000) in the presence of various acids (at a constant concentration of 0.3 M/dm^3) on Fe(III) ion flotation is presented in Fig. 1(A). The collector concentration in the feed suspension was 2×10^{-4} M/dm^3 and the iron concentration was 10^{-4} M/dm^3. From Fig. 1(A) it can be seen that iron removal increases with increasing thiocyanate concentration. It is most evident when the $[SCN^-]/[Fe^{3+}]$ ratio increases up to 2000. Then, the removal of iron from "acid-free medium" at pH 3.5 (i.e., acid was added only to the stock solution of Fe^{3+}) increases from ~40 to ~90%. However, in the presence of acids, the removal decreases as follows: H_2SO_4 > HNO_3 > HCl > H_3PO_4 > $HClO_4$ (e.g., when thiocyanate concentration reaches ~0.4 M/dm^3 and acid concentration of 0.3 M/dm^3 is constant, removal in

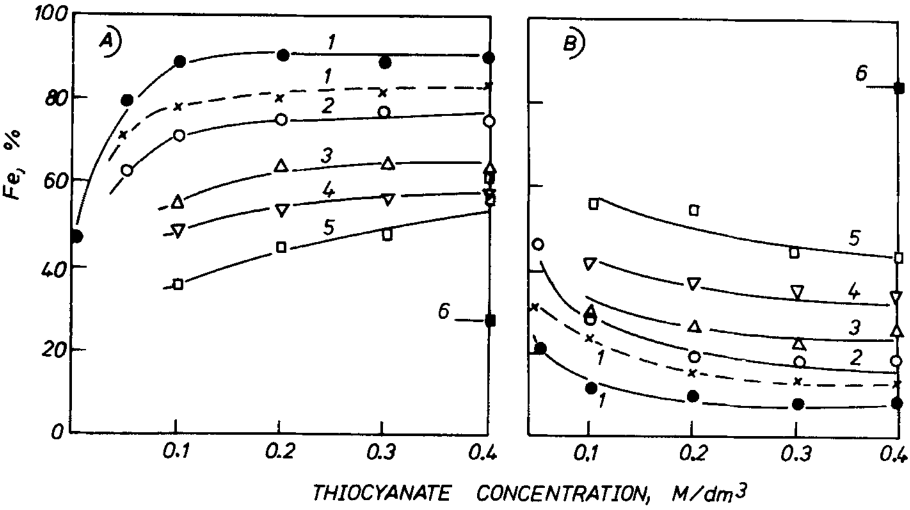

FIG. 1. Influence of thiocyanate concentration and nature of acid (whose concentration of 0.3 M/dm^3 was constant) on Fe(III) removal by ion flotation (Fig. A) and on the amount of Fe(III) in the solution remaining after sublate precipitation (Fig. B): (1) pH ≈ 3.5 (solid line) and pH 2 (dotted line), (2) H_2SO_4, (3) HNO_3, (4) HCl, (5) H_3PO_4, (6) $HClO_4$.

the presence of perchloric acid is the lowest, reaching ~25%, while removal in the presence of sulfuric acid reaches ~70%).

Figure 1(B) illustrates the effect of thiocyanate concentration in the presence of various acids on the percent of Fe(III) remaining in solution (in the supernatant) after sublate precipitation under flotation conditions, but before flotation. From the figure it can be seen that an increase of thiocyanate concentration up to 0.2 M/dm^3 decreased iron concentration in the supernatant up to 10% (i.e., the sublate amount increases). The iron concentration in the supernatant in the presence of acids increases in the following sequence: $H_2SO_4 < HNO_3 < HCl < H_3PO_4 < HClO_4$.

Then the effect of acid concentration on Fe(III) removal from thiocyanate medium was studied. The results obtained are presented in Figs. 2(A) and 3(A) for 0.1 and 0.4 M/dm^3 of thiocyanate, respectively. From these figures it appears that iron removal decreases with increasing acid concentration. On comparing the removals in Figs. 2(A) and 3(A), it is found that the acid effect on the removal is more significant at lower thiocyanate concentration, i.e., greater than 0.1 than for 0.4 M/dm^3. The dependence of the removal on the nature of acids changes as follows: $HClO_4 < H_3PO_4$ (when $[SCN^-] = 0.1\ M/\mathrm{dm}^3$) $< HCl < H_3PO_4$ (when $[SCN^-] = 0.4\ M/\mathrm{dm}^3$) $< HNO_3 < H_2SO_4$. For example, when $[SCN^-] = 0.1\ M/\mathrm{dm}^3$, the removal from "acid-free suspension" (at pH 3.5) reaches ~90%, whereas when $[HA] = 0.6\ M/\mathrm{dm}^3$, the removal is ~70% for H_2SO_4 and ~15% for $HClO_4$. However, at a higher thiocyanate concentration (0.4 M/dm^3), the removal at the above-mentioned acid concentration increases about 10%.

In Figs. 2(B) and 3(B) the effect of acid concentration on iron remaining in the solution after sublate precipitation is presented. Both figures indicate that increasing acid concentration causes an increase in iron concentration in solution (i.e., sublate precipitation decreases). In its dependence on the nature of the acid, the concentration of iron remaining in the solution increases as follows: $H_2SO_4 < H_3PO_4$ (when $[SCN^-] = 0.4\ M/\mathrm{dm}^3$) $< HNO_3 < HCl < H_3PO_4$ (when $[SCN^-] = 0.1\ M/\mathrm{dm}^3$) $< HClO_4$. On comparing the removal of Fe(III) (Figs. 1A–3A) with its precipitation as a sublate (Figs. 1B–3B) it is found that a direct correlation between these parameters exists.

The surface properties of cetyltrimethylammonium surfactant with different counterions media are illustrated by Fig. 4 which presents the influence of potassium salts (chloride and thiocyanate) and ammonium perchlorate concentration on the surface tension (δ, Curves 1–4) and changes of the electric surface potential (ΔV, Curves 5 and 6) of the medium in relation to thiocyanate concentration. Both parameters increase with increasing thiocyanate concentration (the surface tension

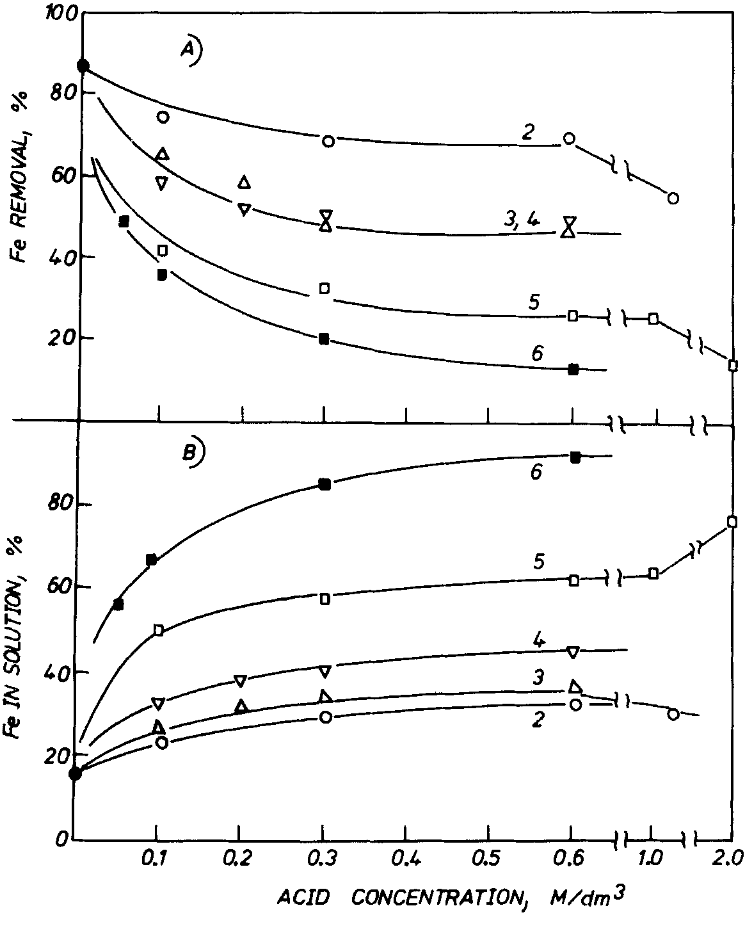

FIG. 2. Influence of acid nature and concentration on Fe(III) removal by ion flotation (Fig. A) and on the amount of Fe(III) in solution after sublate precipitation (Fig. B). Thiocyanate concentration of 0.1 M/dm^3 was constant. Symbols as in Fig. 1.

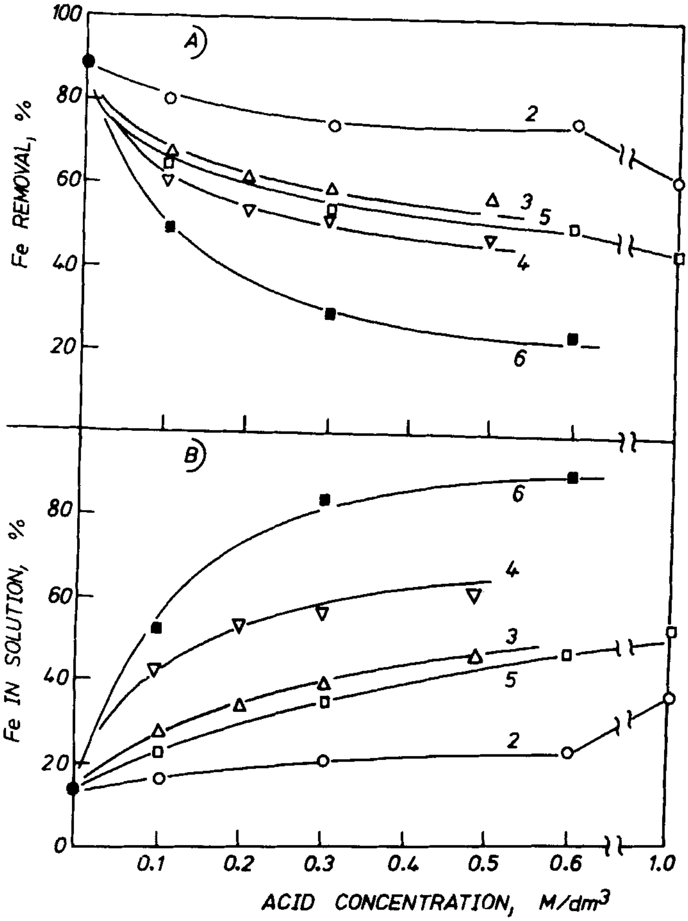

FIG. 3. Influence of acid nature and concentration on Fe(III) removal by ion flotation (Fig. A) and on the amount of Fe(III) in solution after sublate precipitation (Fig. B). Thiocyanate concentration of 0.4 M/dm^3. Symbols as in Fig. 1.

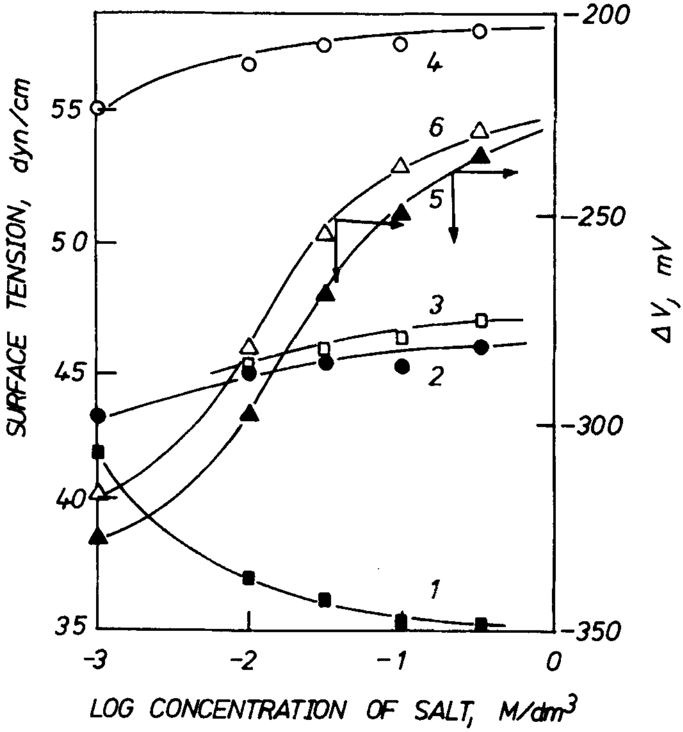

FIG. 4. Influence of inorganic salts concentration on the surface tension (Curves 1-4) and on ΔV (the electric surface potential, Curves 5 and 6) of cetyltrimethylammonium surfactant media. (1) Chloride, (2 and 5) thiocyanate, (3 and 6) Fe(III)-thiocyanate, (4) perchlorate.

also increases with increasing perchlorate concentration), while increasing chloride concentration decreases surface tension. At salt concentrations $>5 \times 10^{-2}$ M/dm^3 (i.e., in the flotation range), the surface tension increases in the following order: $\text{Cl}^- < \text{SCN}^- < \text{SCN}^-\text{-Fe}^{3+} < \text{ClO}_4^-$ (e.g., at salt concentration of 10^{-1} M/dm^3 it reaches ~35 dyn/cm for Cl^-, ~45 dyn/cm for SCN^-, and ~60 dyn/cm for ClO_4^-).

Figure 5 presents the change of foaming properties of cetyltrimethylammonium collector medium: Fig. 5(A) shows their dependence on thiocyanate concentration (no acid); Fig. 5(B), in the presence of various acids under the conditions $[\text{HA}] = [\text{SCN}^-] = 0.2$ M/dm^3. The initial collector concentration in the solution was 2×10^{-4} M/dm^3. From Fig. 5(A) it appears that the foaming properties of the medium decrease as thiocyanate concentration increases. Foaming changes as follows in

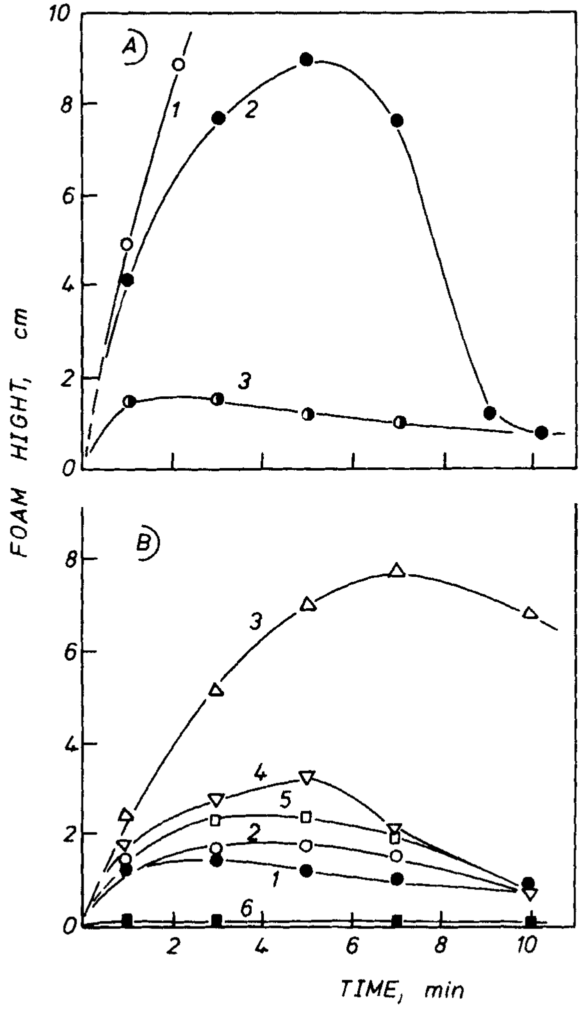

FIG. 5. The effect of thiocyanate concentration (Fig. A, Curves: (1) 0.002, (2) 0.02, and (3) 0.2 in M/dm^3) and nature of acid (Fig. B, $[SCN^-] = [HA] = 0.2\,M/dm^3$, symbols as in Fig. 1) on foam stability.

the presence of acids (Fig. 5B): $HClO_4$ < without acid < H_2SO_4 < H_3PO_4 < HCl < HNO_3.

Next, the effectiveness of Fe(III) solvent extraction under the flotation conditions using ethyl acetate was studied. In Fig. 6 the influence of thiocyanate concentration on extraction effectiveness is presented. It appears from the figure that together with the increase in the thiocyanate concentration up to 0.4 M/dm^3, the removal of Fe(III) by extraction increases and it depends on the nature of acids in the medium. From analysis of the figure it can be estimated that the effect of acids on Fe(III) extraction increases in the following way: H_3PO_4 < H_2SO_4 < HNO_3, $HClO_4$, HCl. For example, when $[SCN^-] = 0.4\ M/dm^3$, in the presence of HCl, HNO_3, or $HClO_4$ the extraction reaches ~70%, whereas with the "acid-free medium" (pH 3.5) the extraction equals ~20%.

The effect of acid concentration on iron extraction is presented in Fig. 7 (Fig. 7A for $[SCN^-] = 0.1\ M/dm^3$ and Fig. 7B for $[SCN^-] = 0.4\ M/dm^3$). The effectiveness of iron flotation and precipitation under these conditions is presented in Figs. 2 and 3. Figure 7 shows that with an increase in

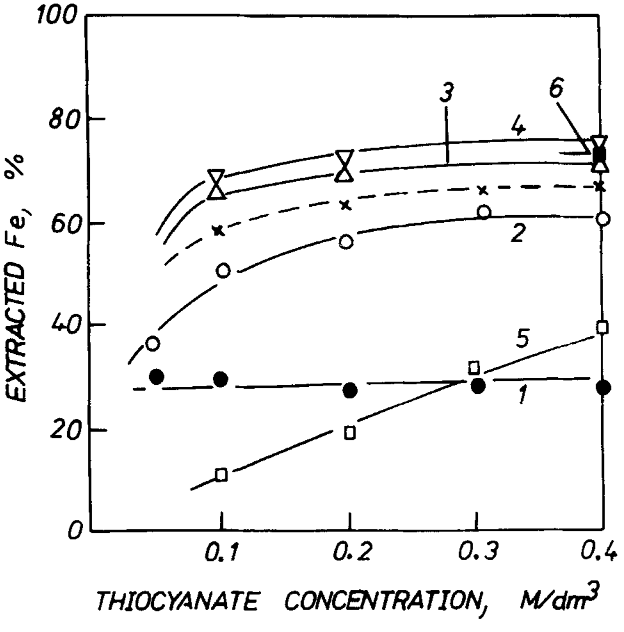

FIG. 6. Influence of thiocyanate concentration and nature of acid (at constant acid concentration of 0.3 M/dm^3) on the extraction of Fe(III) with ethyl acetate. Symbols as in Fig. 1.

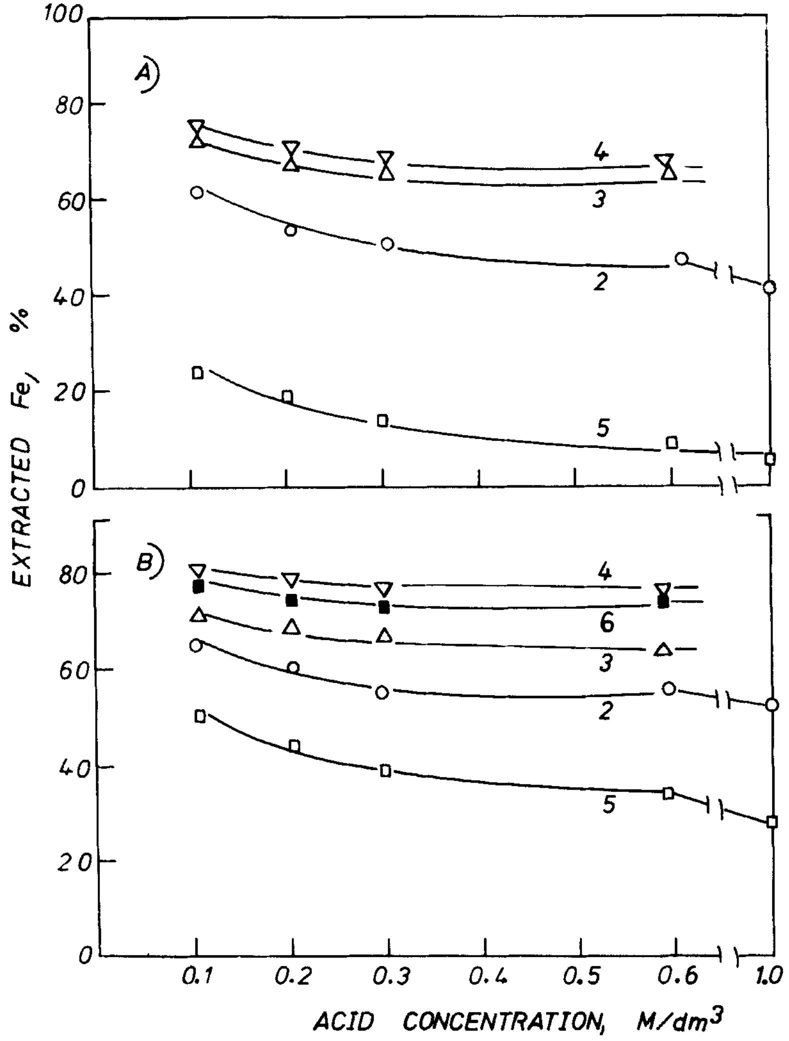

FIG. 7. Influence of acid nature and concentration on the extraction of Fe(III) from thiocyanate solutions: Fig. A, thiocyanate concentration 0.1 M/dm^3; Fig. B, thiocyanate concentration 0.4 M/dm^3. Symbols as in Fig. 1.

acid concentration, the extraction effectiveness decreases. It is most evident when [HA] increases up to 0.3 M/dm^3. However, the negative effects of acids (particularly H_3PO_4) on the extraction decrease when thiocyanate concentration increases (compare Fig. 7A for 0.1 M/dm^3 and Fig. 7B for 0.4 M/dm^3 of thiocyanate).

Figure 8 presents the extraction of Fe(III) from the suspensions remaining after flotation. Figure 8(A) presents data obtained after flotation, the results of which are shown in Fig. 1(A) as a function of thiocyanate concentration; and Fig. 8(B), after flotation, the results of which are shown in Fig. 3(A) as a function of acid concentration. An examination of Fig. 8(A) indicates that the extraction of Fe(III) increases with thiocyanate concentration only in H_3PO_4 medium and in relation to the nature of acid changes as follows: $H_3PO_4 < H_2SO_4 < HNO_3 < HCl < HClO_4$. However, Fig. 8(B) indicates that the extraction percent is nearly constant when HCl and HNO_3 concentration increases, whereas it increases together with increasing $HClO_4$ concentration, and decreases with increasing H_2SO_4 and H_3PO_4 concentration.

DISCUSSION

It has been shown (*31–41*) that in aqueous solutions of Fe(III) and thiocyanate there is formed a mixture of various ferric thiocyanate complexes of the thiocyanate anion with coordination numbers from 1 to 6: simple hydrated Fe^{3+} cations, complex cations $Fe(SCN)^{2+}$ and $Fe(SCN)_2^+$, neutral complex $Fe(SCN)_3$, and complex anions $Fe(SCN)_m^{(-m+3)}$, where $3 < m \leqslant 6$. Excess of one complex form and transformation of one into another depends largely on reacting component concentration, solution acidity, and the presence of a nonaqueous solvent (e.g., alcohol). Under favorable conditions (e.g., concentration) it is possible to obtain an excess of one form. It follows from the data reported by Tarasiewicz (*41*) that an $[SCN^-]/[Fe^{3+}]$ ratios of 333, 666, 3333, and 6666 the complex anions concentration/simple cations + complex cations concentration ratios are 0.3, 1.5, 69.4, and 472.5, respectively. In the present investigations the excess of thiocyanate concentration over Fe(III) concentration changed from 500 to 4000, i.e., it is within the above presented values. Thus, these data may be the basis of further considerations on flotation (or extraction) medium structure. From the above data it can be seen that under the condition $[Fe(III)] \ll [SCN^-]$, the complex equilibria tend to favor increasing proportions of complex anion species having the greater numbers of coordinated thiocyanate anions. Recall that the collector was introduced as a

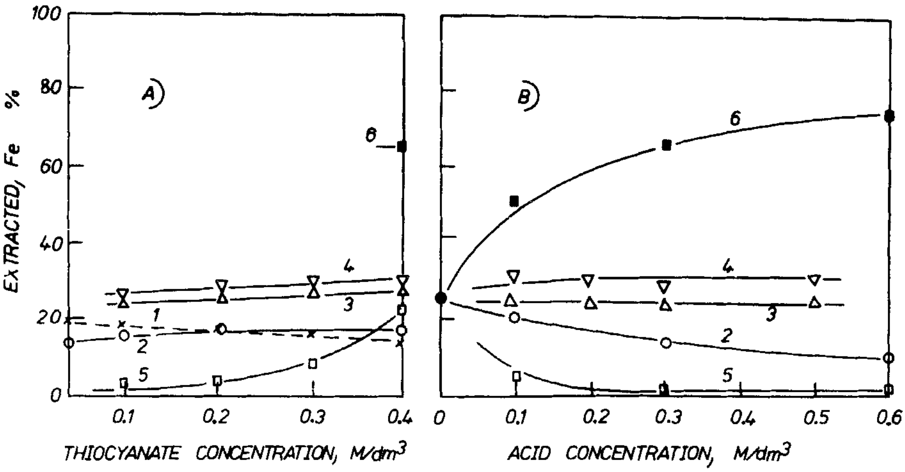

FIG. 8. Extraction of Fe(III) with ethyl acetate from the suspensions remaining after flotation: Fig. 8(A), flotation results are shown in Fig. 1(A); Fig. 8(B), flotation results are shown in Fig. 3(A). Symbols as in Fig. 1.

methanol solution. Then, at a collector concentration of 2×10^{-4} *M*/dm^3 in the flotation medium, the corresponding methanol concentration was 2%, which additionally decreased the dielectric constant of the solution, thereby decreasing dissociation and dehydration of the complex (*38, 39*). This in turn shifted the complex equilibrium toward formation of ferric-thiocyanate complex anions among which there can be found red-colored $Fe(SCN)_6^{3-}$. This property was found applicable in the qualitative and quantitative analysis of Fe(III) (*31, 37–41*).

The collector ought to be oppositely charged to the ion to be removed (the colligend), so in these investigations the cationic surfactant $C_{16}H_{33}N^+(CH_3)_3,Br^-$ was used as a collector for ferric-thiocyanate complex anions. After introducing the collector into the solution containing ferric-thiocyanate complexes, precipitation of red alkylammonium ferric thiocyanate salt (the sublate) was observed. This fact indicates that the predominant form of counterions of $C_{16}H_{33}N^+(CH_3)_3$ cations in the sublate is $Fe(SCN)_6^{3-}$ and that Fe(III) is precipitated in this form the most effectively of all. Increasing the thiocyanate concentration in bulk solution would increase the amount of sublate in the flotation medium. From Fig. 1(B) it appears that the increase of thiocyanate concentration (i.e., the increase of iron complexation) causes decreased Fe(III) concentration in solution (i.e., sublate iron increases). Consequently, Fe(III) removal as the collector–colligend product by ion flotation increases too, as shown in Fig. 1(A). This is in agreement with the conclusions of Walkowiak (*30*), Walkowiak and Grieves (*48*, *49*), Charewicz and Gendola (*50*), and our earlier studies (*51*, *52*) that the cationic surfactant is selective for metal complex anions in preference to Br^- and in preference to SCN^-. The direct effect of the amount of surfactant–colligend precipitate and particles size on the extent of iron flotation was also studied by Grieves et al. (*53*) and Walkowiak (*30*).

To determine the changes in surface properties of the sublate suspension, the surface tension and surface electric potential (ΔV) were measured (Fig. 4, Curves 3 and 6). As can be seen from the figure, δ and ΔV of the suspensions increase with increasing thiocyanate concentration; the change of these parameters is similar to that of the degree of metal complexation produced by the change in thiocyanate concentration. At the thiocyanate concentration for which iron precipitation and removal with cetyltrimethylammonium collector are the highest, both the surface tension and the surface electric potential are also the highest. Experiments also indicate that quaternary ammonium salt particles are formed in solution without metal, in the presence of SCN^- or ClO_4^- anions, and that δ and ΔV (Fig. 4, Curves 2, 4, and 5) of the suspension increase with increasing concentration of these anions (value for ClO_4^- > than for Fe^{3+}-SCN^- > than for SCN^-). However, in the presence of potassium chloride the precipitate particles are not observed, and the surface tension of the solution is at a minimum and decreases with increasing salt concentration (Fig. 4, Curve 1). This bears some connections with the statements by Jurkiewicz (*52*), Grieves et al. (*53–55*), Moore and Phillips (*56*), Waligóra and Steczko (*57*), Czarnecki et al. (*58*), and Rodakiewicz (*59*) that complex formation with a cationic surfactant increases in the order: $Cl^- < SCN^- < ClO_4^-$. From these facts it may be postulated that precipitation of cetyltrimethylammonium salts as a result of exchange of counterions Br^- for SCN^-, $FE(SCN)_m^{(-m+3)}$, and ClO_4^- causes the surfactant soluble form (i.e., ionic pair R_4N^+,Br^-) concentration to decrease in the bulk suspension and at the suspension/gas interface. This causes a decrease of the foam heigh with increasing concentration of thiocyanate, as can be seen from Fig. 5, and also a decrease in the hydration of foam (*52*). Low and relatively dry foam is stabilized by sublate particles. This phenomenon is profitable in ion flotation because it gives a high enrichment ratio (concentration of metal in a foam phase/concentration of metal in the residual suspension).

The initial pH of Fe(III) salt feed solution was ~3.5, so the hydrolysis of iron(III) leads to the formation of iron basic salts or even ferric hydroxide [the precipitate just begins to form at pH 2.6 (*16*, *60*)]. Based on this, one may assume that the bulk of the iron removal from the suspension of pH ~3.5 is due to precipitate flotation of hydroxide (or basic salt). Introduction of thiocyanate and hydrogen ions into this suspension results in iron complexation by thiocyanate, which causes a decrease in the amounts of basic salt and hydroxide (*37–41*). From Figs. 1–3 it appears that the removal and precipitation of Fe(III)-thiocyanate species with cetyltrimethylammonium surfactant are strongly influenced by the nature and concentration of the acids. We assume that the presence of acid may cause these parameters to decrease through: (a) increasing the concentration of H^+ cations which results from pK_{HA} and acids concentration, and (b) introducing other anions coming from acids into the iron–thiocyanate–collector medium. To make this clear, the removal sequence was compared with the acid strength sequence [H_3PO_4 $pK = 2.1, 7.2, 12$; H_2SO_4 $pK = 0.4, 1.92$; HNO_3 $pK = -2$; HCl $pK = -3$; $HClO_4$ $pK = -8$ (*60–62*)]. Except for phosphoric acid, the positions of the other acids in the above series correspond to their negative effects on iron removal (Figs. 1A–3A) and on its precipitation (iron concentration increases in solution, Figs. 1B–3B). This suggests that a strong acid introduced into thiocyanate medium causes a decrease in the number of complex ferric-thiocyanate anions being able to bind with the collector. This probably results from the fact that the presence of an acid stronger than HSCN [i.e., phosphoric < HSCN $pK = 0.85$ < remaining acids (*60–62*)] reduces or even suppresses dissociation of thiocyanic acid; therefore, the concentration of free ligands for iron complexation is reduced in the solution. Nondissociated molecules of HSCN can join the quaternary ammonium thiocyanate (*38, 39, 51, 63–67*), forming adducts of quaternary ammonium thiocyanate with additional thiocyanic acid. Molecules of other acids [particularly H_3PO_4, because, e.g., at pH ~2 about 50% of the H_3PO_4 exists as nondissociated molecules (*26*, *62*)] can be joined to quaternary salts in an analogous way. Due to this, a part of the surfactant ceases to be effective in binding iron–thiocyanate anions. To make this more clear, the removal sequence was compared with Edwards' nucleophilicity function of acid anions: Cl^- −3, NO_3^- −0.4, SO_4^{2-} 3.73 (*63–65*). It appears that there exists a direct correlation between removal and Edwards' nucleophilicity function.

Iron removal and its precipitation are the lowest in the presence of $HClO_4$. This may result, on one hand, from the great strength of this acid, but on the other hand it may be caused by the strong affinity of ClO_4^- anions for long-chain organic cations. Based on the foam fractionation and anion hydration data, Grieves and The (*54*), Grieves et al. (*55*), and Moore and Phillips (*56*) determined the selectivity sequence of the anions studied to be: $Br^- < NO_3^- < SCN^- < ClO_4^-$ using ethylhexadecyldimethylammonium bromide, and in perchlorate solution the precipitation of white alkylammonium perchlorate was observed. Due to this fact, a part of the collector ceases to be effective in binding to ferric-thiocyanate anions (amount of sublate and removal decrease, Figs. 1–3). This results in a surface tension increase (Fig. 4) and a decrease in foaming properties (Fig. 5). Other authors [e.g., Grieves and Bhattacharyya (*9*, *10*), Walkowiak (*30*), Grieves et al. (*68*), Lusher and Sebba (*69*)] also found that the presence of neutral salts decreases the efficiency of ion flotation when using a cationic collector because of the competition for the collector between the colligend and the added anions.

Based upon the order of iron salt stability in an aqueous solution in the presence of the anions studied [taken from the literature data (*60*, *62*)], it appears that Fe(III) phosphate [the predominant form of phosphate anions in the studied medium is $H_2PO_4^-$ (*26*, *62*)] complex stability is lower only than that of hydroxide. It follows that phosphate anions may replace thiocyanate anions in iron complex formation. This replacement of thiocyanate anions with phosphate anions is more effective with increasing phosphate concentration, i.e., higher phosphate/thiocyanate concentration ratios (*37–40*). This fact was found applicable in analytical chemistry, e.g., during the determination of cobalt with thiocyanate, H_3PO_4 is added to prevent red coloring from the accompanying trace amount of iron in solution (*37*, *40*). Because of the very high Fe(III) concentration in the supernatant of the sublation experiment (Figs. 1B–3B) and the very low ion flotation (Figs. 1A–3A) in the presence of H_3PO_4, it may be concluded that iron phosphate does not form compounds with cetyltrimethylammonium surfactant.

From Figs. 6 and 7 it appears that the increase of thiocyanate concentration (i.e., the increase of iron complexation) causes increased Fe(III) extraction, similar to ion flotation of Fe(III) and its precipitation (Figs. 1A and 1B). This suggests that the ferric–thiocyanate anion complex formation reaction is essential for iron removal both by solvent extraction and ion flotation. The characteristics of the complex equilibria of Fe(III) with thiocyanate and the reactions taking place in aqueous solution (in aqueous phase) were given earlier in the discussion of ion flotation results. The second phase (organic phase) in the extraction investigations was ethyl acetate, which belongs to the oxo-solvents possessing an oxygen atom with a pair of electrons which is able to form a donor-acceptor bond with iron and water molecules [e.g., Houghton (*70*) and Schott (*71*)]. The problem of chromatography of metal thiocyanate complexes with oxo-solvents (alcohol and ketones) was studied by Przeszlakowski (*33*, *34*) and Mańko and Soczewiński (*35*, *36*), and the extraction of metals by oxo-solvents was studied by Różycki (*31*), Morrison and Freiser (*39*), Libuś (*72*), Kopacz (*73*), and Haneczkowska

(*74*). From these papers it appears that ethyl acetate molecules can effectively compete with water molecules in iron solvation. Due to this action the red ferric-thiocyanate complexes pass into the ethyl acetate phase from the aqueous phase according to the hydration-solvation mechanism as the complex acid $\{[H(H_2O)_n \cdot q\text{Solv.}]^{3+}, Fe(SCN)_6^{3-}\}$. Ethyl acetate molecules can also effectively compete with water molecules in sublate solvation and, if solvation is strong enough, sublate also passes into the ethyl acetate phase. Thus, we observed both ferric thiocyanate anions (colligend) and cetyltrimethylammonium ferric thiocyanate salt (sublate) extraction.

Curve 1 in Figs. 6 and 7 shows that Fe(III) extraction from suspension at pH ~3.5 is the lowest. The reason for this may be that hydrolysis of iron salt takes place at this pH and that basic salts and hydroxide are not extracted, but flotated significantly (Figs. 1–3, Curve 1). Increasing the thiocyanate concentration in the bulk solution increases the amount of ferric thiocyanate instead of that of basic salts (hydroxide), thereby increasing the percent extraction.

On taking into consideration the acid strength (at constant concentration, e.g., 0.3 M/dm^3) and extraction results (in Figs. 6 and 7), it is found that the effectiveness of extraction increases with increasing acid strength [with lowering pK_{HA} values (60–62)], in contrast to ion flotation and sublate precipitation (in Fig. 1). This suggests that under conditions where $[Fe(III)] \ll [SCN^-]$ and at small differences in thiocyanate and acid concentrations in the aqueous phase, the weakening of thiocyanate dissociation by acids does not significantly influence the amount of ferric thiocyanate complex anions in the aqueous phase, nor does it influence the effectiveness of Fe(III) extraction by ethyl acetate. This is substantiated by the fact that at lower thiocyanate concentration (Fig. 7A for 0.1 M/dm^3 and Fig. 7B for 0.4 M/dm^3), extraction effectiveness in the presence of stronger acids than thiocyanic is reduced.

On taking into account the presence of mineral acids in the ferric thiocyanate medium, not only complex ferric thiocyanate acid but also simple mineral acids may be extracted by ethyl acetate according to the hydration-solvation mechanism as an ion pair $\{[H(H_2O)_n \cdot q\text{Solv.}]^+, A^-\}$. Figure 7 shows that increasing the acid concentration causes decreasing Fe(III) extraction; therefore, it may be connected with competitive extraction of a simple mineral acid and a complex ferric thiocyanate acid. Besides, the negative effect of acid concentration increase on iron extraction may be a result of a concentration increase of anions coming from the acid in the aqueous phase. These anions can combine with cetyltrimethyalammonium cations as well as with iron, as shown in the discussion of ion flotation and sublate precipitation. Contrary to Fe(III) ion flotation and sublate precipitation, surfactant binding by acid anion or excess acid [as nondissociated acid molecules (*63–67*)] does not affect iron extraction negatively because iron thiocyanate complexes are also extracted without a surfactant into an ethyl acetate phase (*31–41*, *63–65*, *70–74*). It is obvious from the opposite influence of perchloric acid on the effectiveness of Fe(III) extraction (Figs. 6 and 7, Curve 6) as compared to its influence on Fe(III) flotation (Figs. 1A–3A, Curve 6). Owing to the strongest affinity of ClO_4^- anions for R_4N^+ cations, cetyltrimethylammonium perchlorate, the most difficult to dissolve, is precipitated (*52–58*), which does not affect iron extraction efficiency negatively (extraction efficiency is very high) but flotation effectiveness is very low. This has been confirmed by the results of extraction from the suspension of $HClO_4$ remaining after flotation (Fig. 8, Curve 6) because the extraction effectiveness is the highest while flotation effectiveness is the lowest (Figs. 1A and 3A, Curve 6).

Anions coming from acid may affect iron extraction, competing with thiocyanate ligand in metal complexing. This is shown by the sequence of stability increases in Fe(III) combinations with different anions as discussed earlier [based on combination stability data given by Lurie (*60*) and Inczedy (*62*)]: nitrates < perchlorates < chlorides < sulfates < thiocyanates < phosphates < hydroxide. Therefore nitrate, perchlorate, and chloride anions are the weakest competitors with thiocyanate in Fe(III) complexing, so their effect on extraction is the smallest. However, sulfate and even more so phosphate anions compete with thiocyanates, inhibiting ferric thiocyanate complex extraction. The greater the phosphate anion concentration and the lower the thiocyanate concentration, the lower is the percent extraction. The flotation results show that ferric phosphate complexes do not form a sublate with cetyltrimethylammonium cations, but from the extraction results it can be seen that they are not extracted by ethyl acetate. This has been confirmed by other authors (*37–40*) who came to the conclusion that in Fe(III) extraction, chlorides and nitrates may be present in the solution, but not sulfates, and particularly not phosphates, because they hinder the process of extraction.

CONCLUSIONS

Fe(III) flotation and extraction possess some common features, although they are governed by different mechanisms. The essential conditions for these processes to take place is Fe(III) complexation by thiocyanate. Hence, the results of this study point to a direct correlation between iron removal by ion flotation or extraction and iron complexation by thiocyanates. For this reason the negative effect of anions coming from mineral acids on flotation or extraction may be associated with their competition with thiocyanate for Fe(III) complexation. Thiocyanate and phosphate iron compounds are characterized by the highest stability of all; thus the removal of iron by flotation and extraction from thiocyanate medium is the lowest in the presence of phosphate anions. The reason for the negative effect of other acid anions on Fe(III) flotation is more complex, as they can compete with ferric thiocyanate anions in the formation of sublate with cetyltrimethylammonium surfactant; this was distinctly observed in the presence of perchlorate anions. However, it does not affect Fe(III) extraction because thiocyanate complexes are also extracted by ethyl acetate (oxo-solvent) without a surfactant.

In this investigation, both ferric thiocyanate anion and cetyltrimethylammonium ferric thiocyanate sublate extraction were observed. Thus, ferric thiocyanate removal by a solvent sublation method into an oxo-solvent layer also ought to be effective.

From the change of the solution surface properties, cetyltrimethylammonium bromide takes part both as a collector of ferric thiocyanate anions (and is their precipitation reagent) and a foam-forming agent (foam is a means for transporting sublate out of a flotation column); for this reason an increase in the activity of cetyltrimethylammonium surfactant is one respect causes its decrease in activity in another respect.

Acknowledgment

The author wishes to thank Mrs L. Holysz for her assistance with the experimental program. The work was financially supported by grant MR I-14.

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Received by editor September 25, 1986
Revised January 23, 1987