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# Precipitate Flotation Studies with Monolauryl Phosphate and Monolauryldithiocarbamate

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# Precipitate Flotation Studies with Monolauryl Phosphate and Monolauryldithiocarbamate

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## Abstract

Monolauryl phosphate has been employed for the removal of copper(II), manganese(II), and zinc(II) by foam flotation at various pH's and ionic strengths. Good removals of all three metal ions were obtained in the basic pH range and in the presence of up to 0.2 *M* sulfate. Coprecipitation of Zn(II) with ferric hydroxide was essential to attain good removal of Zn(II). The removal of Cu(II) was also good from solutions containing oxalate, silicate, phosphate, and metaphosphate; however, the presence of EDTA hinders the removal of Cu(II). The potential of lauryldithiocarbamate as a chelating surfactant for the removal of Cu(II) was explored at various pH's and in the presence of various anions. We conclude that lauryldithiocarbamate is a weak chelating agent, unable to compete efficiently for Cu(II) with anions such as $CO_3^{2-}$, $HPO_4^{2-}$, $SiO_3^{2-}$, and EDTA. The relatively rapid decomposition of lauryldithiocarbamate in solution coupled with its weakness as a chelating surfactant make it unsuitable for the removal of Cu(II) by foam flotation.

## INTRODUCTION

Concern has grown in recent years over the removal of toxic metals from industrial wastewater, and foam flotation techniques appear promising at the bench and pilot-plant scale for the removal of metals and some anions from wastewaters and dilute ore leachates. The literature has been recently reviewed (*1–4*). We applied precipitate and adsorbing colloid flotation to remove toxic metals from a number of wastewaters and simulated wastewaters (*5–9*). Chelating compounds have been explored as surfactants by our group (*8, 9*) and others (*10, 11*); interest in their

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use arises from their capability to form complexes with the desired metal ions in the presence of ions which show strong interference in the removal of metal ions by foam flotation using ordinary surfactants such as sodium laurylsulfate (NLS). Many industrial wastewaters are of relatively high ionic strength, and the detergents found in these wastes often contain phosphates and/or silicates. Chelating agents such as EDTA form stable soluble complexes with metallic ions in the wastewater, making removal with, say, NLS totally ineffective.

In our continuing effort to explore the potential of novel surfactants we report here on the precipitate flotation of copper(II), manganese(II), and zinc(II) with monolauryl phosphate at various pH's and ionic strengths. Monolauryl phosphate is able to remove copper(II) by foam flotation from aqueous solutions containing sulfate, oxalate, silicate, phosphate, metaphosphate, and EDTA. We then explore the potential of lauryldithiocarbamate to chelate copper(II) and remove it by foam flotation at various pH's and in the presence of various anions which show interference in the removal of Cu(II) by flotation using NLS.

## MONOLAURYL PHOSPHATE

Numerous papers have appeared in the literature discussing the use of alkyl phosphates as extractants for transuranium, rare earth, and transition metals. Tri-*n*-butyl phosphate (TBP) is used extensively in the purification and separation of transuranium metals industrially (*12*); also, the industrial extraction of rare earths has been reported (*13*). Radiation stability, relative stability in acidic media, and specificity render TBP uniquely well suited for the extraction of chemically similar metals such as the transuranium elements (*14*). Acidic organophosphates have been used in laboratory studies for the extraction of a wide variety of metals. Radiation stability and chemical stability (more than TBP) make them more efficient in extracting metal species from acidic media; unfortunately, the short alkyl chain acids show little discrimination toward chemically similar metals. Szabo et al. reported good extraction of uranium with mono- and dicaprylphosphoric acids, but the purity of the uranium product was unsatisfactory (*15*). Recently di-long chain alkyl phosphoric acids have been employed in extraction studies; compounds such as di-*n*-decyl, di-ethyl hexyl, and di-*n*-octylphosphoric acids were used (*16*, *17*). In contrast to the numerous studies reported using tri- and dialkyl phosphates, extractions with monoalkyl phosphoric acid are few in number (*18*).

The phosphoric acid esters result from the partial or complete substitution of aliphatic or aromatic groups for the hydrogen atoms of phosphoric acid. The esterification reaction, however, usually is not carried out with phosphoric acid due to poor yield and excessively slow rate, but rather with a more active pentavalent compound such as phosphorus oxychloride, phosphorus pentoxide, or phosphorus pentachloride.

Monoalkyl phosphoric acid preparation requires the use of a 1:1 ratio of alcohol to phosphorus oxychloride with little or no heating, followed by hydrolysis according to

$$\mathrm{ROH} + \mathrm{POCl_3} \rightarrow \mathrm{RPO_2Cl_2} + \mathrm{HCl}$$

$$\mathrm{RPO_2Cl_2} + 2\mathrm{H_2O} \rightarrow \mathrm{RPO(OH)_2} + 2\mathrm{HCl}$$

However, formation of the dialkyl phosphoric acid requires the use of a 2:1 ratio of alcohol to phosphorus oxychloride and mild heat (40–100°C), followed by hydrolysis. The presence of a weak base such as pyridine or triethylamine enhances the rate of reaction and eliminates the need for heat, especially in the preparation of aryl or trialkyl phosphates (*19*).

The dissociation constants for the first acidic hydrogen of the monoalkyl phosphoric acids are larger (the $pK_{a_1}$ values are smaller) than the constant for the dissociation of the first hydrogen of phosphoric acid, and the second dissociation constants are larger than the second constant of phosphoric acid; for example, for monomethyl phosphoric acid $pK_{a_1}$ is 1.54 (*20*) (1.52) (*21*) and $pK_{a_2}$ is 6.31 (6.58) (*21*) compared to 1.97 and 6.82 for $pK_{a_1}$ and $pK_{a_2}$ of phosphoric acid, respectively. The dissociation constants for both the first and second dissociation become smaller in ascending the homologous series of mono-substituted acids; for example mono-*n*-butyl phosphoric acid $pK_{a_1}$ and $pK_{a_2}$ are 1.89 and 6.84, respectively, compared to the values of the methyl homolog values shown above. The dialkyl phosphoric acids are quite strongly acidic, and stronger than the corresponding monoalkyl phosphoric acids; for example, $pK_{a_1}$ are 1.29 and 1.72 for dimethyl phosphoric acid and di-*n*-butyl phosphoric acid, respectively (*20*). As in the case of the mono-substituted acids, the dissociation constants for the disubstituted compounds become smaller in going from dimethyl to dibutyl phosphoric acid; i.e., the acid strength decreases with an increase in *n*-alkyl chain length.

The functional grouping $>\mathrm{P(O)OH}$ is common to mono- and dialkyl phosphoric acids. The fundamental properties of this grouping are a negligible tendency toward the formation of an intramolecular hydrogen bond and a marked tendency toward intermolecular hydrogen bonding (*22*). Due to the presence of both electron donor and electron acceptor groups in this moiety, it is typical of all acidic organophosphates to undergo various specific interactions like self-association and molecular complex formation with diluents or other solutes which might be in solution with the phosphate. Freezing point studies (*23–25*), isopiestic measurements (*24*, *26*), and new infrared spectra (*25*, *27*) have confirmed the fact that the dialkyl phosphoric acids are dimers in nonpolar aromatic and aliphatic diluents and monomeric in alcohols, but both monomer and dimer species are present in chloroform (*16*, *17*).

Monoalkyl phosphoric acids are highly polymeric in aliphatic hydrocarbons and carbon tetrachloride, dimeric in hexane and chloroform, and monomeric in methanol (*16*, *28*). For example, an isopiestic study of molecular weight in benzene showed mono-*n*-decyl phosphoric acid to be polymeric with seven monomers per polymer unit (*28*). Kolarik et al. have studied the self-association of some dialkyl phosphoric acids in aqueous solutions, and found that they dimerize and that there is dependence of the association constant on the nature of the ions contributing to the ionic strength. They concluded that the tendency of di-*n*-alkyl phosphoric acids toward self-association in the aqueous phase increases sharply with *n*-alkyl chain length (*29*).

## EXPERIMENTAL

The foam flotation apparatus used in this work was a batch column essentially identical to that described by Chatman et al. (*7*). House air was passed through Ascarite, water (for rehumidification), and glass wool, then through a "fine" glass gas dispersion tube at the bottom of the column. Air flow rates of about 65 mL/min were used. Practical grade Triton-X-100 (TX100) and hexadecyltrimethylammonium bromide (HTA) were used as carrier surfactants; all other chemicals were reagent grade. Stock solutions (1000 mg/L of the metal ions) were diluted with distilled water and the pH adjusted to the desired value with NaOH solution. Monolauryl phosphate was added, the solution was diluted to 200 mL, the pH was measured, and then the solution was transferred to the flotation column. Carrier surfactant was injected into the column and timing of the run was started. Air flow rates were monitored with a soap film flowmeter and stopwatch. Samples for analysis were withdrawn from the bottom of the column, acidified with nitric acid, and analyzed by atomic absorption spectrophotometry. Analyses for Cu(II), Mn(II), and Zn(II) were carried out at 324.75, 279.48, and 213.86 nm, respectively.

### Preparation of Monolauryl Phosphate

The preparation of monolauryl phosphate was carried out by the procedures of Christensen (*30*) and Plimmer and Burch (*31*) with slight modifications as follows: 30 mL anhydrous ether was placed in a 100-mL round-bottom flask, 11.21 mL (0.05 mol) lauryl alcohol was added, and the mixture was stirred for 2 min to make the solution homogenous. 5mL (about 0.05 mol) phosphorus oxychloride was added and the solution was refluxed gently with vigorous magnetic stirring for 2 h. The reflux was stopped while the stirring was continued for 30 min more in order to remove as much as possible of the liberated hydrogen chloride which was trapped in a dilute aqueous solution of sodium hydroxide. After the reaction mixture cooled to room temperature the ether was distilled off under vacuum with a water aspirator at a temperature not exceeding room temperature (24°C). After most of the ether was distilled the temperature was raised to 35°C to ensure complete removal of the ether. To the viscous residue about 40 mL 1.0 *M* NaOH and 60 mL distilled water were added. The Jello-like white solid became less gelatinous and soaplike. Drops of 1.0 *M* NaOH were added to test for complete precipitation. The white soapy solid was not filterable on a sintered glass funnel under vacuum (water aspirator), so the filtration was done by gravity over a 24-h period. The collected solid was left to dry at room temperature for 3 d, then was placed in a desiccator which contained anhydrous calcium chloride and Ascarite; it was left in the desiccator for several days until the solid reached constant weight.

## Characterization of the Phosphate

The infrared spectrum of the compound was recorded from a Nujol mull and from a KBr disk; absorption bands were found at 3200 (broad), 2900, 2850, 2650, 2350 (broad and strong), 2140 (broad), 1960, 1770 (both broad and weak), 1460 and 1380 (medium), 1200, 1140, 1070 (broad and strong), 1020 and 990 (both strong), 940 (broad and strong), 830, 780, and 720 (small shoulders). The band at 3200 $cm^{-1}$ indicates the presence of some water. The other bands were in agreement with the bands observed by Ferraro et al. (*28*) in the infrared spectra of monodecyl phosphoric acid and with the generalized pattern of infrared spectra of monoalkyl phosphoric acids compiled by Thomas (*22*).

The equivalent weight of the compound was determined by titration with sodium hydroxide solution as follows: sodium hydroxide solutions of 0.0969 and 0.0194 *M* were standardized by titration with potassium acid phthalate using a pH meter and glass combination electrode. A 0.103 g sample of the phosphate was weighed and dissolved in 100 mL distilled water. The phosphate did not dissolve completely at room temperature. Heating to 70°C resulted in a turbid solution which remained turbid with no visible solid particles when cooled to room temperature. The pH of this solution was 2.75; the solution was then titrated with 0.0969 *M* NaOH.

Due to the poor solubility displayed by the above phosphate solution, a new solution was made containing 0.0500 g phosphate in 100 mL distilled water. The new solution was clearer than the first one and had a pH of 2.8 before titrating with 0.0194 *M* NaOH solution. Two more phosphate solutions were prepared in this way and titrated similarly with a 0.0194 *M* NaOH solution. A typical titration curve is shown in Fig. 1. As can be seen from the figure, the volume of NaOH needed to reach the second equivalence point is more than double the volume needed to reach the first equivalence point. This we attribute to the presence of some sodium hydrogen lauryl phosphate with the dihydrogen lauryl phosphate. Determination of the amount of sodium by emission photometery was done on a sample of 0.1 g solid dissolved in 4 mL concentrated sulfuric acid and diluted volumetrically to 100 mL with distilled water. This sodium determination showed that 39.6 wt-% of the solid phosphate is present as the monosodium salt and the rest is dihydrogen lauryl phosphate. Using this information, we calculated the corresponding weights of sodium salt in the samples used in the titrations, and the equivalent weight of the sodium hydrogen lauryl phosphate from the difference between double the volume of NaOH used to reach the first equivalence point and the volume determined experimentally for the second equivalence point. Subtracting the weight of sodium salt from the sample weight gives the weight of dihydrogen lauryl phosphate in the sample. From this weight and the volume of NaOH needed for the first equivalence point, the equivalent weight of dihydrogen lauryl phosphate was calculated. The average equivalent weight obtained from the three titrations for dihydrogen lauryl phosphate was 280.4 and for sodium hydrogen lauryl phosphate 309.8. The theoretical equivalent weights are 266.33 and 288.33 for the anhydrous dihydrogen and the sodium hydrogen lauryl phosphate, respectively. Evidently there is a molecule of water per molecule of phosphate.

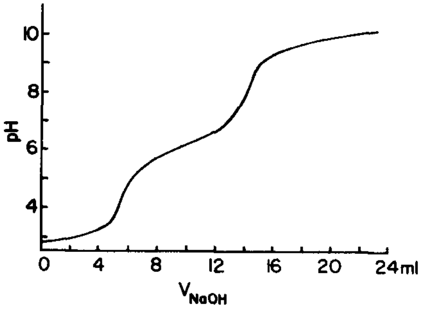


FIG. 1. Titration curve for lauryl phosphate.

As can be seen from the titration curve, the first equivalence point is not as sharp as the second. An attempt to get a clearer equivalence point was made by adding a known amount of $HNO_3$ until the pH of the solution was 1.05. The resulting solution of phosphate and $HNO_3$ was titrated with NaOH by the procedure used in the previous titrations. This titration resulted in a more diffuse first equivalence point. This result indicates that the first hydrogen of the dihydrogen lauryl phosphate is quite acidic, and the diffuse equivalence point is due to increased ionic strength.

## Foam Flotation Studies

The ability of lauryl phosphate to form a foam was tested at various pH's. These tests indicated that no foam is generated at pH's higher than 4.0, and good foam could be generated at pH's less than 3.0.

The stock solution of 1.0 g/L lauryl phosphate forms micelles upon standing at room temperature; therefore, prior to use in foam flotation, the solution was heated to about 70°C to break up micelles. This yielded a homogenous solution which was used for foam flotation studies.

## Copper(II)

Copper(II) (50 mg/L) was precipitated as $Cu(OH)_2$ and floated with monolauryl phosphate using TX100 as the carrier surfactant. Table 1 shows the results. Good removal was obtained whether 25 or 50 mg/L lauryl phosphate was used provided the flotation pH was not $<7.0$. At pH's below 7.0 the flotation was very difficult and excessive amounts of TX100 were needed due to the inability of TX100 to form the foam in the presence of lauryl phosphate. However, as the pH was raised, less and less TX100 was needed to generate the foam. Even with excessive amounts of TX100 the removal at pH's below 7.0 was not very good; for example, at pH 7.0

TABLE 1

Foam Flotation of 50 mg/L Cu(II) with Lauryl Phosphate at Various pH's[a]

| | I | | | | II | | | | |
|---|---|---|---|---|---|---|---|---|---|
| pH 1 | 9.15 | 9.3 | 9.5 | 10.2 | 7.9[b] | 8.9 | 9.35 | 9.5 | 10.15 |
| pH 2 | 7.3 (9.0) | 7.6 | 8.2 | 10.0 | 6.85 | 8.3 | 8.0 | 9.0 | 9.95 |
| Residual Cu(II), mg/L | 1.10 (0.7) | 0.6 | 0.3 | 0.25 | 2.2 | 0.65 | 0.60 | 0.35 | 0.20 |

[a] I: 50 mg/L phosphate. II: 25 mg/L phosphate. 10 min flotation. pH 1: pH before adding lauryl phosphate. pH 2: Flotation pH.

[b] 15 min of flotation. 70 mg/L TX100 needed.

about 3.0 mg/L residual copper concentrations were obtained, and at pH 6.0 the residual copper concentration was about 5.0 mg/L. At pH's higher than 7.5 the foam is generated easily with decreasing amounts of TX100 needed; for example, flotation at a pH of 7.3 required 50 mg/L TX100 whereas at pH of 7.6 and higher 25 mg/L TX100 was sufficient to carry out the flotation. Two blank runs were made at pH's 7.5 and 9.5 in which the copper hydroxide was precipitated following the same procedure with no phosphate added and foamed with TX100. A very small portion of the precipitate was floated after 30 min of flotation. Most of the precipitate remained in suspension in the flotation column.

Coprecipitation of Cu(II) with Fe(III) hydroxide was then carried out followed by foam flotation using the same procedure described above; the Fe(III) was added to the Cu(II) solution prior to the adjustment of pH and the addition of the phosphate. At pH's higher than 7.5 the foam flotation resulted in residual Cu(II) concentrations of 0.25 mg/L whether 50 or 100 mg/L Fe(III) was used to coprecipitate the copper. When 100 mg/L Fe(III) was used to coprecipitate Cu(II), 100 mg/L TX100 was needed to float the precipitate; the TX100 was added in doses of 25 mg/L over a period of 5 min. However, the flotation of copper coprecipitated with ferric hydroxide at pH's of 7.0 or below resulted in residual copper concentrations of more than 1.0 mg/L. For example, when the precipitation pH was 7–6.5 and the flotation pH was 6.3–6.7, a residual Cu(II) concentration of 2.5–2.9 mg/L was obtained. When the flotation pH was 5.7, the residual Cu(II) concentration was 5.6 mg/L. A blank run was carried out in which 50 mg/L Fe(III) was precipitated and floated with TX100 and no lauryl phosphate added. It resulted in a good foam at pH of 7.0 which did not carry the ferric hydroxide precipitate. Another blank run in which 50 mg/L Fe(III) was precipitated and 25 mg/L lauryl phosphate added and floated with 20 mg/L TX100 at pH of 6.2 resulted in a clear solution in the foam flotation column within 1 min.

The effects of ionic strength, and of anions which show strong interference with NLS flotation of metal ions, on the flotation of Cu(II) were examined following the procedure described above. The anions $SO_4^{2-}$, $SiO_3^{2-}$, $C_2O_4^{2-}$, $PO_4^{3-}$, EDTA, or metaphosphate $[(PO_3)_6^{6-}]$ were added to the Cu(II) solution before adjustment of pH or the addition of lauryl phosphate. The results are shown in Table 2. In the presence of sulfate and silicate anions, very good removal was obtained. In the presence of oxalate the removal was not as good. In the presence of EDTA the removal is impaired drastically and the residual Cu(II) concentration obtained corresponds to the amount required to form a 1:1 complex with the EDTA. In the presence of $PO_4^{3-}$, good removal with TX100 as a foaming agent resulted if the $PO_4^{3-}$ concentration was

TABLE 2

Effects of Ionic Strength and Interfering Anions on the Flotation of Cu(II) with Lauryl Phosphate[a]

| $SO_4^{2-}$ | | | | $PO_4^{3-}$ | | | |
|---|---|---|---|---|---|---|---|
| Conc (*M*) | pH 1 | pH 2 | Residual Cu(II) (mg/L) | Conc (mg/L) | pH 1 | pH 2 | Residual Cu(II) (mg/L) |
| 0.025 | 10.0 | 8.8 | 0.5 | 25 | 9.95 | 8.95 | 0.25 |
| 0.05 | 9.6 | 8.6 | 0.6 | 50 | 9.60 | 8.8 | >10 |
| 0.075 | 9.9 | 8.6 | 0.55 | 75 | 9.45 | 8.65 | >10 |
| 0.10 | 9.5 | 8.9 | 0.75 | 50 | 9.5 | 8.6 | 0.5[b] |
| 0.20 | 9.7 | 8.9 | 0.67 | 75 | 9.3 | 8.5 | 0.6[b] |

| $SiO_3^{2-}$ | | | | $C_2O_4^{2-}$ | | | |
|---|---|---|---|---|---|---|---|
| Conc (mg/L) | pH 1 | pH 2 | Residual Cu(II) (mg/L) | Conc (mg/L) | pH 1 | pH 2 | Residual Cu(II) (mg/L) |
| 25 | 9.65 | 8.6 | 0.38 | 25 | 9.65 | 8.6 | 1.8 |
| 50 | 9.7 | 8.7 | 0.3 | 50 | 9.55 | 8.65 | 3.6 |
| 75 | 9.75 | 8.8 | 0.3 | 75 | 9.5 | 8.7 | 4.35 |

| Metaphosphate | | | | EDTA | | | |
|---|---|---|---|---|---|---|---|
| Conc (mg/L) | pH 1 | pH 2 | Residual Cu(II) (mg/L) | Conc (mg/L) | pH 1 | pH 2 | Residual Cu(II) (mg/L) |
| 25 | 9.25 | 8.8 | 0.7[b] | 25 | 9.55 | 8.65 | 5.4 |
| 50[c] | 9.7 | 8.6 | 0.93[b] | 50 | 9.45 | 8.95 | ~10 |
| 75[c] | 9.35 | 8.6 | 2.2[b] | | | | |

[a] Original solution contained 50 mg/L Cu(II), 25 mg/L lauryl phosphate. TX100 as carrier surfactant. pH 1 and pH 2 are the precipitation and flotation pH, respectively.

[b] HTA used as carrier surfactant.

[c] 50 mg/L Fe(III) used for coprecipitation.

25 mg/L; however, when the $PO_4^{3-}$ concentration was 50 and 75 mg/L, TX100 was unable to remove Cu(II) and hexadecyltrimethylammonium bromide (HTA) was needed. With HTA and monolauryl phosphate very good removal of Cu(II) in the presence of $PO_4^{3-}$ was obtained. A foam flotation run in the presence of 50 mg/L $PO_4^{3-}$ was carried out in which no lauryl phosphate was added and HTA was used as surfactant. The residual Cu(II) concentration was $\gg 10$ mg/L.

In the presence of metaphosphate, HTA was needed as carrier surfactant. Good removal occurred when the metaphosphate concentration was 25 mg/L; however, if the metaphosphate concentration was 50 or 75 mg/L, no precipitate of copper hydroxide formed and no visible removal of Cu(II) was observed. Co-precipitation of Cu(II) with 50 mg/L ferric hydroxide in the presence of metaphosphate, followed by foam flotation with HTA, resulted in good removal of Cu(II) [residual Cu(II) concentrations shown in Table 2]. Four foam flotation runs in which no lauryl phosphate was added and the Cu(II) was coprecipitated with 50 mg/L Fe(III) hydroxide in the presence of 25, 50, 75, and 100 mg/L metaphosphate, followed by flotation with 25, 50, 75, and 100 mg/L HTA, respectively, resulted in 0.60, 0.60, 0.70, and 1.85 mg/L residual Cu(II) concentrations, respectively.

## Manganese(II)

The flotation of manganese was carried out following the same procedure used for Cu(II) flotation. TX100 was used as carrier surfactant, and the solution in the foam flotation column was clear within 2–3 min. The flotation was carried out for 15 min. Representative results are shown in Table 3. Very good removal of manganese was obtained at pH 8.5–10.0. At pH's lower than 8.5 the residual manganese concentration was more than 10 mg/L. At pH's higher than 10 the residual manganese concentration was more than 1.0 mg/L when 25 mg/L lauryl phosphate was used; however, when 50 mg/L lauryl phosphate was used the residual manganese concentration was less than 1.0 mg/L.

Coprecipitation of Mn(II) with 50 mg/L Fe(III) hydroxide, following the same procedure as in the absence of Fe(III), but then with the addition of 25 mg/L lauryl phosphate followed by flotation with 50 mg/L TX100 resulted in very good removal at pH's of 8.5 or higher, and the residual Mn(II) concentration was 0.2–0.15 mg/L. This residual Mn(II) concentration is substantially lower than the ~0.5 mg/L obtained in the absence of Fe(III). At pH's of 8.0 or lower, the residual Mn(II) concentration was > 10 mg/L. It is worth mentioning that in alkaline solution in the presence of air some Mn(II) is converted to Mn(III) and $MnO_2$.

The effects of ionic strength and of sulfate as an interfering anion were studied following the same flotation procedure as above. In a series of

TABLE 3

Foam Flotation of Mn(II) with Lauryl Phosphate at Various pH's[a]

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| pH 1 | 8.0 | 8.5 | 9.0 | 9.5 | 9.75 | 10 | 10.3 | 10.2[b] |
| pH 2 | 7.55 | 7.65 | 7.65 | 7.5 | 8.3 | 9.25 | 9.45 | 9.15 |
| Residual Mn(II) (mg/L) | $\gg$10 | 0.6 | 0.45 | 0.6 | 0.85 | 1.10 | 2.55 | 0.75 |

[a] 50 mg/L Mn(II) and 25 mg/L lauryl phosphate in original solution. 25 mg/L TX100. pH 1 and pH 2 are the precipitation and flotation pH, respectively.

[b] 50 mg/L lauryl phosphate.

runs the Mn(II) was precipitated and floated in the absence of Fe(III); in another series the Mn(II) was coprecipitated with Fe(III) hydroxide. Sulfate was present in both series. The results are shown in Table 4. The removal of Mn(II) is better when coprecipitated with Fe(III) hydroxide. It was observed that a longer stirring time was needed in the presence of sulfate when the Mn(II) was precipitated in the absence of Fe(III), and a longer time was needed than was necessary when no sulfate was added.

## Zinc

The procedure for precipitation of $Zn(OH)_2$ and flotation with lauryl phosphate and TX100 was the same which was used for Cu(II) and Mn(II). Precipitation followed by the addition of 25 or 50 mg/L lauryl phosphate and flotation with TX100 of 50 mg/L Zn(II) resulted in incomplete removal at various pH's. The best results were at pH's around 9.0, where the residual Zn(II) was 2.5 mg/L. Coprecipitation of 50 mg/L Zn(II) with 50 mg/L Fe(III) hydroxide followed by flotation with lauryl phosphate and TX100 resulted in complete removal of the brown precipitate of Fe(III) hydroxide, and a white precipitate, presumably of Zn(II) hydroxide, remained in the solution in the foam flotation column. Atomic absorption analysis for Zn(II) in this solution showed a zinc concentration of 2.27 mg/L at pH's of 9.0 and 8.5. Flotation of 25 mg/L Zn(II) coprecipitated with 50 mg/L Fe(II) gave improved removals of Zn(II).

Solutions containing 25 mg/L Zn(II) and 75 mg/L Fe(III) were chosen for flotation studies at various pH's. 25 mg/L lauryl phosphate and

TABLE 4

Effect of Added Sulfate on Flotation of Mn(II) with Lauryl Phosphate and TX100[a]

| | I | | | II | | |
|---|---|---|---|---|---|---|
| $SO_4^{2-}$ conc (*M*) | pH 1 | pH 2 | Residual Mn(II) (mg/L) | pH 1 | pH 2 | Residual Mn(II) (mg/L) |
| 0.025 | 9.0 | 8.2 | 1.0[b] | 9.5 | 8.6 | 0.4 |
| 0.05 | 9.0 | 8.9 | 1.0[b] | 9.5 | 8.8 | 0.4 |
| 0.075 | 9.0 | 9.0 | 1.3 | 9.5 | 8.7 | 0.55 |
| 0.10 | 9.0 | 8.35 | 1.15 | 9.5 | 8.65 | 2.30 |
| 0.20 | | | | 9.5 | 8.3 | 3.50[c] |

[a] I: no Fe(III) added. II: 50 mg/L Fe(III) added. 50 mg/L Mn(II) and 25 mg/L lauryl phosphate in original solution. 50 mg/L TX100.

[b] 35 mg/L TX100.

[c] 75 mg/L TX100.

TABLE 5

Flotation of Zn(II) with Fe(III) and Lauryl Phosphate at Various pH's

| pH 1 | 7.6 | 8.0 | 8.5 | 9.0 | 9.5 | 10 |
|---|---|---|---|---|---|---|
| pH 2 | 7.0 | 7.4 | 7.6 | 8.7 | 8.85 | 9.35 |
| Residual Zn(II) (mg/L) | 8.33 | 3.45 | 1.27 | 0.23 | 0.27 | 0.2 |

TABLE 6

Effect of Added Sulfate on Flotation of Zn(II) with Fe(III) and Lauryl Phosphate[a]

| $SO_4^{2-}$ conc (*M*) | 0.025 | 0.05 | 0.075 | 0.1 | 0.2 |
|---|---|---|---|---|---|
| Flotation pH | 8.95 | 8.85 | 8.8 | 8.9 | 8.85 |
| Residual Zn(II) (mg/L) | 0.25 | 0.35 | 0.8 | 0.57 | 1.13 |

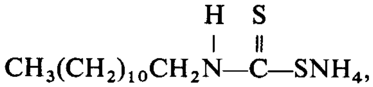
[a] 25, 75, and 25 mg/L of Zn(II), Fe(III), and lauryl phosphate, respectively, in original solution. 50 mg/L TX100. Flotation time 10 min.

50 mg/L TX100 were used. The results are shown in Table 5. Good removal of Zn(II) was obtained at pH's 8.5–10.0. At pH's of 8.0 or lower the removal was not good, probably due to incomplete precipitation of Zn(II) as the hydroxide. The solubility product of $Zn(OH)_2$ is $4.5 \times 10^{-17}$; from this value of the solubility product one concludes that a pH higher than 8.0 is required for precipitation of Zn(II) as the hydroxide. At pH's higher than 10, zinc hydroxide is transformed to the soluble zincate anion, since zinc is amphoteric. No attempt was made to study the removal of Zn(II) at pH's higher than 10.

The effect of adding sulfate to the zinc solution on the removal of Zn(II) by foam flotation with Fe(III) and lauryl phosphate was studied following the same procedure used for Zn(II) in the absence of sulfate. The sulfate was added prior to adjustment of pH and the addition of lauryl phosphate. The pH was adjusted to 9.5 before adding lauryl phosphate. Table 6 shows the results. Good removal was obtained in all cases.

## DITHIOCARBAMATE

Dithiocarbamates are readily obtainable from carbon disulfide, an amine, and a base. When an aliphatic amine is added to a suspension of $CS_2$ in $NH_4OH$, the ammonium salt of the monosubstituted dithiocarbamic acid is formed (*32*, *33*). The salts of dithiocarbamic acids decompose readily if a solution of the salt in water, alcohol, or even acetone is heated to boiling. They also decompose on long standing in aqueous solutions whether the solution is acidic, neutral, or basic; however, the decomposition is slower in basic media (*34*, *35*).



Ammonium dodecyldithiocarbamate, $CH_3(CH_2)_{10}CH_2\overset{\overset{H}{|}}{N}-\overset{\overset{S}{\|}}{C}-SNH_4$, or the sodium salt, was used as a chelating surfactant to remove Cu(II) ions from aqueous solutions by foam flotation. Ammonium and sodium dodecyldithiocarbamate (DDIC) are soluble in ethanol, slightly soluble in distilled water, and more soluble in aqueous 0.1 *M* NaOH solutions. It was found that they dissolve quite well and rapidly in 0.1 *M* ethanolic solutions of NaOH.

DDIC (ammonium or sodium salts) have two peaks at 254 and 290 nm in the ultraviolet spectra of aqueous, ethanolic, aqueous 0.1 *M* NaOH, and 0.1 *M* alcoholic NaOH solutions. Both salts decompose quite rapidly. For example, in aqueous solutions the concentration of DDIC was reduced to about one-fourth the original concentration within 5 min. after preparation; however, in 95% ethanol, aqueous 0.1 *M* NaOH, and alcoholic 0.1 *M* NaOH solutions, DDIC is more stable and about 10–15 min elapsed after preparation of the solution before the concentration reduced to one-fourth the original. Since the UV spectral studies showed that DDIC solutions are unstable, solutions of DDIC in 95% ethanol or 0.1 *M* alcoholic NaOH were freshly prepared for each of the foam flotation runs or precipitation studies.

Precipitation of Cu(II) with DDIC was investigated at various pH's and in the presence of anions which show strong interference with the removal of Cu(II) by foam flotation with sodium lauryl sulfate (NLS); If this provides effective removal, one would anticipate that foam flotation of Cu(II) with DDIC should also be effective. Solutions were prepared containing 25 mg/L Cu(II) and the desired anion, if any. The pH was then adjusted to the desired value with NaOH solution. While the solution was slowly stirred, DDIC solution was added, the precipitates allowed to settle, and samples of the supernatant liquid were analyzed by atomic absorption at 324.7 nm for Cu(II).

An olive green precipitate was obtained at pH's greater than 7, whereas an olive green solution was obtained at pH's $<7.0$. The precipitate changed color to yellow and then to black at pH's $>10$. Satisfactory levels of Cu(II) in the supernatant liquid were obtained at pH's 7.5–11 in the absence of interfering anions. However, in the presence of $NO_3^-$, $CO_3^{2-}$, $SiO_3^{2-}$, $HPO_4^{2-}$, and EDTA, copper concentrations of more than 1.0 mg/L in the supernatant liquid were obtained. Increasing the amount of DDIC in solution from 50 to 100 mg/L did not improve the results in the presence or absence of interfering anions.

On the basis of these results, foam flotation runs were carried out on solutions containing 25 mg/L Cu(II) at pH's in the range 7–11.5. The same flotation procedure used for lauryl phosphate was followed in this investigation. Very sparse foams of height 1–2 cm were obtained from solutions containing 50 to 100 mg/L DDIC in the foam flotation column. This foam is inadequate to provide separation, so a carrier surfactant was needed.

Flotation runs at pH's 6.5–10.0 using NLS as carrier surfactant resulted in good foam which did not carry the precipitate completely from the solution in the flotation column. HTA was also incapable of removing the precipitate from solutions in the flotation column. Since the precipitate was not removable by cationic or anionic surfactants, nonionic surfactants were used. With Tween-60 and TX100 the removal was much better; however, nonreproducible results were obtained and the residual Cu(II) concentrations were 0.25–3.0 mg/L in the pH range 7.5–11.5. With these irreproducible results one might increase the amount of DDIC to maintain enough DDIC in solution after some has decomposed. 50, 62.5, and 100 mg/L DDIC in solution gave the same levels of removal; increasing the amount of DDIC did not improve the removal.

If the pH of Cu(II) solution was 7–11.5 before adding DDIC, flotation resulted in $>10$ mg/L residual Cu(II) concentrations. If the pH was adjusted with ammonia solution in the above pH range, the same residual Cu(II) was obtained ($>10$ mg/L).

## CONCLUSIONS

Very good removal of Cu(II) precipitated as the hydroxide followed by flotation with lauryl phosphate was obtained at pH's of 7–10. At pH's below 7.0 the flotation was difficult and more carrier surfactant (TX100) was needed. When Cu(II) was coprecipitated with ferric hydroxide and floated with lauryl phosphate, good removal was also obtained in the above-mentioned pH range. At pH's below 7.0 the removal was comparable to that obtained by flotation in the absence of ferric hydroxide. Probably good removal can be attained if the molar ratio of Fe:Cu is increased to 3:1 or 4:1. Excellent removal was obtained in the presence of sulfate, silicate, and phosphate; however, in the presence of EDTA the removal was not good. In the presence of metaphosphate the precipitation of Cu(II) hydroxide was hindered and coprecipitation with ferric hydroxide was necessary. The removal of Cu(II) in the presence of metaphosphate, where Cu(II) was coprecipitated with ferric hydroxide, was good with HTA, and the presence of lauryl phosphate was not necessary (its presence does not affect the removal).

Mn(II) can be removed successfully by flotation with lauryl phosphate in less than 10 min of flotation and without the excessive alkaline aeration needed in the flotation with $Fe(OH)_3$ and NLS, or LIX65. Only 15 min of moderate stirring, followed by the addition of lauryl phosphate, was enough to induce good removal by foam flotation. The removal of Mn(II) in the presence of up to 0.1 *M* sulfate was good, especially if the Mn(II) was coprecipitated with ferric hydroxide. The removal of Zn(II) was successful when Zn(II) was coprecipitated with ferric hydroxide in the ratio Fe:Zn of 2 or more and at pH's 8.5–10. Aluminum hydroxide might also be a good coprecipitant for zinc. In the presence of 0.2 *M* sulfate, the removal was very good.

DDIC is a weak chelating agent, at least for copper. It cannot displace other complexing agents such as $NH_3$, EDTA, $HPO_4{}^{2-}$, $SiO_3{}^{2-}$, or $CO_3{}^{2-}$ as indicated by the precipitation study in the presence of these anions. In terms of cost, instability, and inability to compete with common complexing agents, we are forced to conclude that it is not a promising surfactant for foam flotation work.

From the present study we conclude that lauryl phosphate is much better than NLS, dithiocarbamate, or LIX reagents in removing transition metal ions from aqueous solution. The ease of preparation is an added advantage of lauryl phosphate over the other surfactants.

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