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Precipitate Foam Flotation of Copper, Nickel, Cobalt, and Manganese with LIX Reagents

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Abstract

The precipitate flotation of copper, nickel, cobalt, manganese, zinc, and cadmium with LIX65 and LIX63 (hydroxyoxime compounds) and carrier surfactants hexadecyltrimethylammonium bromide and TX100 was investigated. The effects of pH and possibly interfering ions (sulfate, phosphate, EDTA) were studied. LIX65 was found to give good results with copper, nickel, cobalt, and manganese; LIX63 was less satisfactory.

INTRODUCTION

Solid ion-exchangers are widely used for the removal of undesired ions from solutions and for separating ionic species from each other. Careful choice of the resin and eluting solution(s) has made many otherwise difficult separations successful; however, solid ion exchangers have some characteristics which make their use in industry rather limited. For example, the backwash requirement and the void volume render their continuous countercurrent operation rather difficult (*1*). Also, if the concentration of one or more of the ions in the mother liquor is high, separation is poor.

Liquid–liquid extraction is another well-known separation technique applied in the chemical laboratory as well as in industry. In this separation method the preference of a chemical species for one solvent over another is utilized; the two solvents must be immiscible. This method is not effective in separating quite similar chemical species.

Liquid ion exchange can be looked upon as a solvent extraction process

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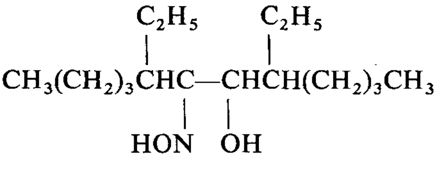
in which the preference of the chemical species for a certain solvent is enhanced by the presence of a chelating agent in the solvent into which the chemical species is to be extracted. One can also look at the liquid ion exchange process as simple ion exchange (*1*). For example, in the extraction of copper from aqueous solutions by LIX reagent, copper ions are exchanged for hydrogen ions. The copper ions eventually appear in the organic layer while the hydrogen ions are released into the aqueous phase (*2*). Liquid ion exchange is not hindered by several of the difficulties encountered in solid ion exchange process and the time requirement is much less.

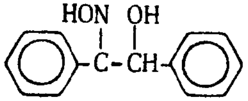
For a substance to be able to function as a liquid ion exchanger, two main requirements must be fulfilled. The molecule must contain an ion exchange group and at the same time have such a large nonpolar part that it is practically insoluble in aqueous phases (*3*). To minimize loss of reagent, the liquid ion exchanger is generally dissolved in an inert solvent which has negligible solubility in water. The first liquid ion exchangers were amines dissolved in an inert solvent such as xylene. They have been used to remove mineral or carboxylic acids from aqueous solutions. Also they have been used to extract metals in anionic form ($ZnCl_4^{2-}$ and MnO_4^-, for example) from aqueous solutions (*1*). Alkyl phosphoric and sulfonic acids are also in use as liquid cation exchangers.

General Mills produced the first commercial chelating extractant under the trade name LIX63; it was designed for the selective extraction of copper from dilute leach liquors. This reagent is an aliphatic α-hydroxy oxime.



$$CH_3(CH_2)_3\overset{\overset{C_2H_5}{|}}{C}H\underset{\underset{HON}{|}}{C}{-}\underset{\underset{OH}{|}}{C}H\overset{\overset{C_2H_5}{|}}{C}H(CH_2)_3CH_3$$

Later several modifications of salicylaldoxime were introduced as aromatic liquid ion exchangers under the trade names LIX64, LIX64N, LIX65N, LIX70, LIX71, and LIX73. All these LIX reagents are derived from 2-hydroxybenzophenone oxime (*4*).



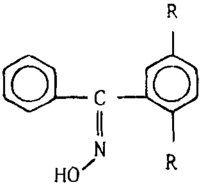
Other liquid ion exchangers selective for copper have been introduced by other companies (*4*, *5*).

Commercial LIX63 is a light yellow liquid containing up to 70% inert solvent. It is insoluble in water ($<1 \times 10^{-5}$ *M*) (*6*) and contains 5,8-

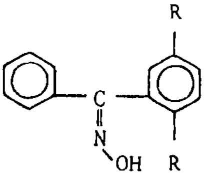
diethyl-7-hydroxy-dodecan-6-one oxime as the active component (*7*). It has been used to extract copper from leach liquors in laboratory and pilot plants; it has not been used for commercial purposes due to insufficient discrimination for copper over ferric iron (*4*). Attempts to precipitate the active component in LIX63 by sodium or potassium hydroxide were unsuccessful. The term LIX63 will be used here to refer to the active component of commercial LIX63. Ashbrook has purified LIX63 by column chromatography on alumina, which yielded an off-white waxy material pure by TLC (*8*). Tammi has purified LIX63 by complexation with copper or nickel, and claimed that he obtained the two isomeric forms, syn and anti, of LIX63 (*9*). Fritz and co-workers have prepared LIX63 by reacting the parent ketone with hydroxyl amine and obtained a viscous liquid (*10*). IR, NMR, UV and mass spectra of LIX63 have been reported (*8*, *9*). LIX63 has been reported to form a green precipitate with copper(II) which has a molar ratio of 1:1 Cu:LIX63 (*9*). Fritz et al. (*10*), have found LIX63 to form a green 1:1 precipitate with copper(II) at oxime concentrations below 0.1 *M* with loss of two protons, and a brown 1:2 Cu:LIX63 at higher oxime concentrations with loss of the hydroxyl proton but not the oxime proton. Sudderth and Jensen have found a blue precipitate of LIX63–copper sulfate in their extraction studies with the as-received LIX63 (*11*). With nickel a 1:3:1 (Ni:LIX63:SO_4^{2-}) blue complex has been reported by Tammi in his Ni-complex method of purifying LIX63 (*9*).

The commercial LIX65N reagent is an amber liquid containing up to 40% inert solvent; it is insoluble in water (1 × 10^{-5} *M* for pure LIX65N) (*6*). It forms water-insoluble complexes with metallic cations. The Cu–LIX65 complex is completely soluble in solvents of LIX65N up to 7.5 g/L copper at 20°C. The LIX65N reagent is quite stable and its solutions in acetone are stable for more than a year (*12*). The term LIX65 will be used here to refer to the pure active component of commercial LIX65N.

Ashbrook (*13*) has isolated LIX65 and found it to be 2-hydroxy-5-nonylbenzophenone oxime. LIX65 exists in two isomeric forms, anti (active) and syn (inactive).



anti-isomer of LIX65

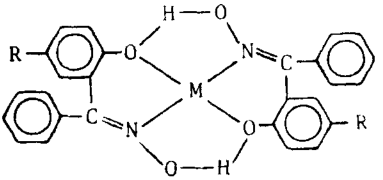


syn-isomer of LIX65

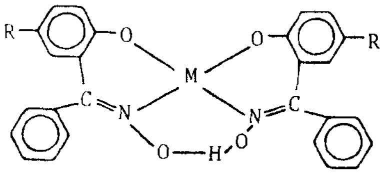
R = C_9H_{19}

At equilibrium they are in the ratio anti:syn of 80:20%. The anti-isomer is a yellow-brown viscous liquid which forms a complex with copper(II) quite rapidly. The syn-isomer is a white crystalline solid which forms no complex with copper(II) at low pH's. At high pH the syn-isomer becomes active and forms a complex with copper. The as-received LIX65 reagent is 1.02 *M* in the anti-isomer and has a ratio of 5.4:1 anti:syn.

The copper(II)–LIX65 complex has been reported to be CuL_2, where L = LIX65 and has Structure I (*14*).



I



II

Pratt and Tilley have confirmed the formation of a CuL_2 complex and found evidence of the formation of CuL^+, $[Cu_2L_2]^{2+}$, and $[Cu_2L[^{3+}$ complexes at high copper(II) concentrations (*15*). The structure of the Cn^{II}, Ni^{II}, and Pd^{II} complexes of salicylaldoxime (SALO) are found to be of Type I, whereas the complexes of SALO with Co^{II}, Zn^{II}, Fe^{II}, and Mn^{II} are of Type II (*4*). It is expected that SALO and LIX65 metal complexes are similar in structure (*4*).

Removals of Cu(II) from water samples by floc foam flotation using $Fe(OH)_3$ and sodium lauryl sulfate (NLS) have been successful at pH's around 6.5, but the separation becomes marginal at ionic strengths above 0.25 M (*16*). The presence of anions such as phosphate, oxalate, or EDTA in the aqueous solution hinders the removal of Cu^{II} using NLS (*17*, *18*). The removals of Ni(II) and Co(II) by means of the same procedure used for Cu(II) were rather poor even in the absence of interfering anions (*19*). Removals of Mn(II) as MnO_2 by the procedure used for Cu(II) or as MnS with hexadecyl trimethylammonium bromide (HTA) and CuS were not successful either (*19*). A number of other studies using chelating flotation agents have been reported. Removal of Hg(II) and Ed(II) by ion flotation has been studied by Okamoto and Chou (*20*). Nagaraj and Somasundaran have used LIX63 and LIX65N to carry out the flotation of the copper minerals cuprite (Cu_2O) and chrysocolla ($CuSiO_3$) (*21*, *22*); they list a number of pertinent earlier references. Raghavan and Fuerstenau investigated the oil extraction and flotation of hematite with octylhydroxamate (*23*).

In the present work the removals of Cu(II), Ni(II), Co(II), and Mn(II) by precipitate foam flotation with LIX63 and LIX65 have been studied, and the ability of LIX63 and LIX65 to precipitate these metal ions in the presence of EDTA, phosphate, sulfate ions, and ammonia has been investigated.

EXPERIMENTAL METHODS

Purified LIX63 and LIX65 were dissolved in acetone at concentrations of 10 g/L. Metal ion stock solutions [Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II)] of 1.0 g/L were prepared. One molar solutions of sulfate and nitrate were prepared from the sodium salts. Solutions of disodium EDTA (0.001 *M*), phosphate (1 g/L), hexadecyltrimethylammonium bromide (1 g/L), and the nonionic surfactant Triton X-100 (5 g/L) were prepared in distilled water.

The apparatus used for foam flotation was a simple batch-type column previously described (*16*). An Aztec Mark II atomic absorption spectrophotometer and a Sargent-Welch Model LSX pH meter with a combination glass electrode were used. Analyses were carried out by atomic absorption spectrophotometry for copper (324.7 nm), nickel (232.0 nm), cobalt (240.7 nm), and manganese (279.5).

Purification of LIX Reagents

The purification of LIX65 was done by the procedure described by Ashbrook (*13*) and Atwood and Miller (*14*) as follows. One hundred milliliters of as-received LIX65 was placed in a 500-mL separatory funnel, to which was added slowly 30 mL of 25 wt-% NaOH solution to form a yellow-orange precipitate of the sodium salt of LIX65. A test for complete precipitation was done by adding extra drops of sodium hydroxide solution. The organic and aqueous layers were discarded and the precipitate washed 6 times with 20–25 mL portions of hexane. Two hundred milliliters of hexane was then added to the funnel and about 200 mL of 25 vol-% H_2SO_4 was added slowly until the precipitate had completely dissolved. The aqueous acid layer was separated and discarded, and the organic layer was washed twice with 25 mL portions of distilled water. The hexane was evaporated, leaving a yellow-brown viscous liquid which was left exposed to the air at room temperature for several days to insure that all the hexane had evaporated. About 50 g of LIX65 was obtained. The purity was checked by TLC as described below.

LIX63 was first purified by column chromatography as follows (*8*). A chromatographic column was packed with chromatographic alumina, and the column was wetted with methanol. Five milliliters of as-received LIX63 was placed in the column; the column was drained until the level of liquid was 1–2 mm above the alumina, and then eluted with acetone. The first 75 mL of eluate collected was discarded because it contained the oily solvent of LIX63 in addition to LIX63. Eluate was collected thereafter; about 700 mL was collected. The eluate was tested for LIX63 by adding to 1–2 mL a few drops of Cu(II) solution and of 1.0 *M* NaOH, and checking for the greenish color of the LIX63–Cu(II) complex. The acetone–LIX63 solution was evaporated under vacuum to a volume of about 30 mL. This solution was left exposed to air at room temperature for 3 days to permit the remaining acetone to evaporate; about 5 mL of odorless very viscous liquid, LIX63, was left. This viscous liquid was pure by TLC as described below.

Column chromatographic purification of LIX63 did not conveniently give sufficient quantities of the compound to do the planned studies of foam flotation and precipitation of metal ions. The nickel complexation method described by Tammi (*9*) was therefore used. Thirty milliliters of as-received LIX63 was stirred with 30 mL of 1.0 *M* $NiSO_4$; 2.4 mL of 30 wt-% NaOH solution was then added slowly over a period of 4 h. The organic layer was dark brown in color. The two layers were separated and the aqueous layer was discarded. The organic layer was stirred in contact with 30 mL of aqueous solution containing 0.5 *M* $NiSO_4$ and 1.5 *M* H_2SO_4 for 0.5 h. A blue precipitate formed and floated over the aqueous layer. The mixture was filtered under vacuum, and the blue precipitate was washed four times with acetone and left to dry in air at room temperature for 2 days. Eight grams of dry blue nickel complex was obtained.

The complex was placed in a beaker, 30 mL 1.0 *M* HNO_3 and 40 mL ether were added, and the mixture was stirred for 1.5 h. The two layers separated. The aqueous layer was discarded, and the organic layer was washed twice with 10 mL portions of distilled water. The ether was evaporated at room temperature over a period of 2 days. A waxy off-white solid (6.446 g) was obtained.

The purity was checked with TLC and compared with the sample prepared by column chromatography as follows (*24*). Commercial silica gel sheets of Chromatogram 6060 (Eastman Kodak) were used, and the developing solvent was 96:4% toluene:ethyl acetate. About 5 mL of developing solvent was placed in the developing jar and left to equilibrate for 3–4 h. Spots of the desired-solutions were placed 1.5 cm above the rim of the silica gel TLC plate, 1 cm away from the edge of the plate, and 1 cm apart. The plate was then placed in the developing jar. When the solvent front reached the end of the plate, the plate was taken out and left to dry for a few minutes and then examined under a UV lamp. The distances traveled by each component and by the solvent front were measured. For LIX65 purified according to the procedure above, two spots of almost equal size were observed with R_F values of 0.11 and 0.616. For LIX63, the sample prepared by chromatographing on alumina gave one spot having $R_F = 0.48$; the sample purified by the Ni-complex method gave one spot with the same R_F as that of the sample obtained by column chromatography.

Procedures for Precipitation Studies

Procedure a. Four-milliliters of stock solution of the desired metal ion was placed in a 100-mL beaker, distilled water was added, and while the solution was stirred magnetically the pH was adjusted to the desired value with NH_3 or NaOH solution. Then 0.8 (1.6) m*L* LIX stock solution was added and the solution diluted to the 80-mL mark on the beaker. The solution mixture contains 50 ppm metal ion and 100 (200) ppm LIX. The solution mixture was then vigorously stirred for 20–30 min; stirring was then reduced and eventually stopped after about 10 min. The pH was measured again and the solution mixture left to settle. The next day the supernatant liquid was analyzed by atomic absorption for the metal ion under study.

Procedure b. Four milliliters of stock solution of the desired metal ion was placed in a 100-mL beaker and distilled water added. To 0.8 (1.6) mL LIX stock solution drops of NH_3 or NaOH solution were added to adjust the solution to the desired pH; the solution was mixed well and transferred to the beaker containing the metal ion while the solution was rapidly stirred. The solution was diluted to 80 mL, the pH was checked, and the resulting solution [which contained 50 ppm metal ion and 100 (200) ppm LIX] was stirred vigorously for 20–30 min. The rest of the procedure is as in Procedure *a* above.

Procedures for Foam Flotation Studies

Procedure c. Ten milliliters of stock solution of the desired metal ion was placed in a 250-mL beaker and distilled water was added. While the solution was rapidly stirred the pH was adjusted to the desired value with NH_3 or 0.1 and 1.0 *M* NaOH solution. Two (4) milliliters of LIX stock solution was added while maintaining vigorous stirring. The solution was then diluted to 200 mL. The resulting suspension was stirred vigorously for 20–30 min and then the stirring was reduced and eventually stopped to permit coagulation of the precipitate. The pH was measured again and the suspension transferred to the foam flotation column. The column air flow rate was adjusted to 60–67 mL/min prior to the transfer. The solution was aerated for 0.5 min, by which time most of the precipitate was in the sparse foam (2–3 cm high) produced by the LIX reagent. One to 1.4 mL TX100 stock solution (or 5 mL HTA) was injected into the column and the timing was started. (At that point the solution contained 25–35 ppm TX100 or 25 ppm HTA.) Samples were withdrawn from the column, acidified with concentrated HNO_3, and stored for analysis by atomic absorption for the metal ion under study. In some cases additional amounts of surfactant (TX100 or HTA) were injected into the column; this will be indicated, whenever it was done, in the Results section.

Procedure d. Ten milliliters of stock solution of the desired metal ion was placed in a 250-mL beaker and diluted with distilled water. Two (4) milliliters of LIX stock solution was placed in a small beaker, to which drops of NH_3 or NaOH solution were added with mixing; this was then transferred to the beaker containing the metal ion. Distilled water was used to dilute the solution to 200 mL, the pH was measured, and the suspension was stirred vigorously for 10–15 min, then stirred slowly for 10 min. The rest of this procedure is identical to Procedure *c* above.

Procedure e. Ten milliliters of metal ion stock solution was placed in a 250-mL beaker and distilled water was added. If the pH was below 5, it was adjusted with NH_3 or NaOH solution to 5–6.5. With vigorous stirring 2 mL LIX solution was added and then 1 drop of NaOH or NH_3 added to bring the pH to 6.5–8.0. The solution was stirred vigorously for 10 min and the pH was adjusted to the desired value. It was stirred vigorously for an additional 10 min [25–35 min in the case of Mn(II)] while the pH was monitored, then stirred slowly for another 10 min. The pH was measured again and the suspension foamed as in Procedure *c* above.

RESULTS WITH LIX65

LIX65 did not produce much foam even in the absence of metal ions when it was introduced to the foam flotation column. A sparse foam about 1–4 cm high was produced when the solution contained 25 ppm LIX65. The foam was higher at higher pH's. A carrier surfactant was therefore needed to carry the solid particles away from the solution in the foam flotation column.

Copper(II)

Precipitation and foam flotation of copper(II) were carried out with

LIX65 and solutions of $Cu(NO_3)_2$ and $CuSO_4$. The precipitation studies were aimed at finding out the pH range expected to be best for foam flotation, in addition to determining if a precipitate forms at all or if just a turbid liquid solution is produced at the pH in question. Early work in this study revealed that a fairly dilute stock solution of LIX65 in acetone (1000 ppm) is not good for studies on copper(II) due to the solubility of the copper–LIX65 complex in acetone; this problem was eliminated when a 10-g/L solution of LIX65 in acetone was used. The early studies also showed that the reaction of LIX65 with copper(II) in the pH range 6–11 is rather slow; it takes about 10 min before the green color of the Cu–LIX65 predominates over the blue color of hydrated Cu(II) even with vigorous stirring. Vigorous stirring was necessary for breaking up any particles of $Cu(OH)_2$ which form, thus making it easier for the LIX65 to complex with Cu(II) and displace the hydroxide ions. Stirring is also necessary to facilitate the contact of LIX65 molecules with Cu(II) since LIX65 is relatively insoluble in water and tends to stay at the surface of the aqueous solution.

Studies of the precipitation of Cu(II) by LIX65 were carried out following Procedures *a* and *b* described above. The copper sulfate stock solution was used as the copper(II) source. Concentrated and dilute ammonia solutions were used to adjust the pH. The suspensions were made up to contain 50 ppm Cu(II) and 200 ppm LIX65. The results are shown in Table 1. When Procedure *b* was followed in the precipitation studies, the green color predominated immediately after the LIX65–NH_3 mixture was added. This indicates that LIX65 can compete effectively with ammine ligand and hydroxide ion. Procedure *a* results indicate that LIX65 can displace the hydroxide and ammine ligands quite effectively at the pH's shown in Table 1.

Foam flotation studies were carried out following Procedures *c* and *d*. NH_3 and NaOH were used to adjust the pH of the solution. Twenty-five

TABLE 1

Precipitation Study of Cu(II) with LIX65

Procedure *a*			Procedure *b*	
pH		Cu(II) in supernatant liquid (ppm)	pH	Cu(II) in supernatant liquid (ppm)
Before[a]	After[b]			
7.3	6.9	1.26	6.45	8.07
8.25	8.10	0.53	8.35	0.3
9.20	9.15	0.53	9.45	0.38
			10.05	0.25

[a] Before: pH before adding LIX65.

[b] After: pH after LIX65 was added.

ppm of TX100 was used to generate a carrier foam, since the foam generated by the LIX65 was not extensive enough to carry the precipitate up and away from the solution in the foam flotation column. Table 2 shows the results of foam flotation following Procedures *c* and *d* with NH_3 or NaOH solutions used to adjust the pH. The results indicate that LIX65 can compete effectively with NH_3 ligand up to a pH of 9.5. It becomes less effective as the pH is increased above 10. When NaOH was used to adjust the pH, there was a considerable drop in pH after adding LIX65, especially at the lower pH values, but such a change occurred to a lesser extent when NH_3 was used to adjust the pH in Procedure *c*. This could be attributed to NH_3-NH_4^+ buffering.

We note that the same residual Cu(II) concentrations resulted whether 100 or 200 ppm LIX65 was used in the original solution. Pratt and Tilley (*15*) have studied the reaction of Cu(II) with LIX65 in ethanol at pH's 2–4 by UV–visible spectroscopy. They reported four complexes of Cu–LIX65: $Cu(L)_2$, $[Cu(L)]^+$, $[Cu_2L_2]^{2+}$, and $[Cu_2L]^{3+}$, where L = LIX65 which has lost a proton. The last two complexes are expected to form at high Cu(II) concentration. $[Cu_2L_2]^{2+}$ was found to have a formation constant, $k_d = [Cu_2L_2{}^{2+}]/[CuL_2][Cu^{2+}] = 1.7 \times 10^4$ L/mol, at 25°C. CuL_2 was found to have a formation constant $\log \beta_2$ of 26.5 L^2/mol^2. In the solution mixture used in this study, 50 mg/L of Cu(II) and 100 mg/L of

TABLE 2

Foam Flotation of Cu(II) with LIX65[a]

Procedure *c*, NH_3 for pH adjustment			Procedure *c*, NaOH for pH adjustment			Procedure *d*, NH_3 for pH adjustment	
pH before	pH after	Cu(II) ppm	pH before	pH after	Cu(II) ppm	pH	Cu(II) ppm
7.7	7.35	2.3	6.5	6.15	10.7	6.4	3.4
8.15	7.85	0.4	6.75	6.3	5.6	7.5	3.2
8.5	7.7	0.5	7.5	6.95	1.5	8.17	0.43
8.85	8.60	0.55	8.55	8.5[b]	0.35	8.65	0.43
9.05	8.85	0.35	9.0	8.0[b]	0.10	8.9	0.4
9.5	9.4	0.63	9.2	7.5	0.25	9.3[c]	0.88
10.0	9.95	3.60				9.45	0.75
						9.6[c]	0.75
						10.05[c]	1.7
						10.35	~6.0

[a] Original solution contained 50 ppm Cu(II) and 200 ppm LIX65. Cu(II) ppm refers to residual Cu(II). pH before is pH before adding LIX65; pH after is the flotation pH.

[b] pH was readjusted just before foam flotation.

[c] 50 ppm Cu(II) and 100 ppm LIX65 in original solution.

TABLE 3

Effect of Ionic Strength and Interfering Anion on Foam Flotation of Cu(II) with LIX65[a]

$NaNO_3$				SO_4^{2-}				PO_4^{3-}				EDTA			
Conc (*M*)	pH before	pH after	Cu(II) (ppm)	Conc (*M*)	pH before	pH after	Cu(II) (ppm)	Conc (ppm)	pH before	pH after	Cu(II) (ppm)	Conc (ppm)	pH before	pH after	Cu(II) (ppm)
0.025	8.42	7.85	0.6	0.025	8.55	7.75	0.9	25	8.5	7.85	0.4	14.5	8.5	8.0	3.0
0.05	8.4	8.0	0.8	0.050	8.85	8.3	0.65	50	9.05[b]	6.95	1.5	25	8.75	8.4	4.6
				0.10	9.20[b]	7.1	4.0	50	9.3[b]	7.3	3.35	25	9.05	8.88	~6
				0.20	9.20[b]	7.7	4.3	75	9.8[b]	7.15	3.60	25	8.5[b]	7.1	7.36
												50	8.7[b]	7.2	10.9

[a] Original solution contained 50 ppm Cu(II) and 200 ppm LIX65. NH_3 was used to adjust the pH. pH before and pH after refer to the pH before adding LIX65 and foam flotation pH respectively.

[b] NaOH solution was used to adjust the pH.

LIX65 were used, corresponding to molar concentrations of 7.869 × 10^{-4} and 2.932 × 10^{-4}, respectively, for Cu(II) and LIX65. These molar ratios rule out CuL_2 and CuL^+ as the predominant species being formed. It is quite possible that a binuclear or polynuclear complex is being formed.

A solution containing 50 mg/L of Cu(II) and 100 mg/L of LIX65 was made at pH 9.35 following Procedure *c* for foam flotation, and the olive green precipitate was isolated by filtration, washed with distilled water, and left to dry at room temperature for 2 days. Another solution mixture, 7.869 × 10^{-4} *M* in Cu(II) and 1.58 × 10^{-3} *M* in LIX65 (molar ratio of 1:2), was prepared by the same procedure and the brown precipitate was isolated by filtration, washed with distilled water, and left to dry for 2 days. In 100 mL acetone, 0.01 g of each was dissolved. Not all solid dissolved in both cases; brown precipitate was present in the solution made in the 1:2 ratio and green precipitate was present in the other. UV–visible spectra of both solutions were recorded using a Cary Model 14 spectrophotometer. Both solutions gave the same spectrum; the main absorption band was at 350.6 nm. Pratt and Tilley (*15*) reported a band at 350 nm in CCL_4 and acetone for CuL_2 complex; this agreement between our result and theirs indicates that in both solutions CuL_2 complex is present. Solubility studies showed that the precipitate from the 1:2 (Cu:LIX65) mixture is soluble in chloroform, hexane, toluene, and methanol. The precipitate from a solution of the composition as used in the foam flotation studies [(2.7:1) Cu:LIX65 molar ratio] partially dissolves, giving a brown-yellowish colored solution in chloroform and leaving a green precipitate. The green precipitate was isolated and found to be insoluble in chloroform, acetone, hexane, methanol, and aqueous 0.1 *M* HNO_3. These results indicate that more than one kind of complex was formed in the 2.7:1 (Cu:LIX65) molar ratio solution; one of them is probably CuL_2 (from UV–spectra) and the other is possibly a polymer.

The effects of ionic strength and of anions which showed strong interference with Cu(II) removal by floc foam flotation using $Fe(OH)_3$ and

TABLE 4

Precipitation Studies

	Study 1[a]					
pH before	7.3	8.1	8.5	8.95	10.5	11.0
pH after	4.8	5.5	5.1	8.5	9.2	11.0
Ni(II) in supernatant (ppm)	≫10	≫10	≫10	>10	~9.0	~4.0

[a] Original solution contains 50 ppm Ni(II) and 200 ppm LIX65. NaOH used for pH adjustment, Procedure *a*.

[b] 50 ppm Ni(II) and 100 ppm LIX65 in original solution. NaOH used for pH adjust-

NLS (*17*, *18*) were studied following Procedure *c* for foam flotation. The anions SO_4^{2-}, PO_4^{3-}, or EDTA were added to the Cu(II) solution before adjustment of pH or the addition of LIX65. The results are shown in Table 3. Evidently LIX65 can remove Cu(II) from aqueous solution quite well up to 0.05 *M* sulfate concentration; whereas at sulfate concentration of 0.1 and 0.2 *M* the residual Cu(II) concentration is about 4 ppm. Removal is also good up to a phosphate concentration of 50 ppm (5.26×10^{-4} *M*). Removal in the presence of EDTA is not as good as in the presence of phosphate or sulfate anions.

Nickel(II)

Precipitation studies of Ni(II) with LIX65 were done following Procedures *a* and *b*, with sodium hydroxide and ammonia used for pH adjustments. Table 4 shows the results. As the tabulated data indicate, when Procedure *a* was followed the residual Ni(II) concentration in the supernatant liquid is greater than 10 ppm, independent of whether 100 or 200 ppm LIX65 is used or NaOH or NH_3 is used to adjust the pH. Residual Ni(II) concentrations are less than 10 ppm at pH's of 10 or above; of course, that does not rule out the precipitation of nickel as $Ni(OH)_2$ with possibly a surface coating of Ni LIX65 complex. The $Ni(OH)_2$ precipitate is greenish-blue in color whereas the color of the precipitate in the presence of LIX65 is clear green. The supernatant liquid was turbid in precipitation Studies 1, 2, and 3. The results of Study 4 are much better; the residual nickel concentration in the supernatant liquid is about 1.0 ppm at pH's around 10, but at pH 8.5 or below it is more than 10 ppm Ni(II). From this study we can say that LIX65 is incapable of replacing the hydroxide ion totally, whereas the precipitation study with LIX65–base added together (Procedure *b*) shows that LIX65 can compete quite well with the hydroxide ion.

Foam flotation studies following Procedure *c* confirmed the precipitation

of Ni(II) with LIX65

Study 2^b			Study 3^c			Study 4^d			
8.2	8.9	10	7.9	9.05	9.95				
5.5	8.5	9.25	7.6	8.75	9.85	8.55	9.1	10.25	11.35
$\gg$10	>10	~6.0	$\gg$10	>10	~9.0	>10	4.2	1.0	2.0

ment, Procedure *a*.

[c]As in Study 1, NH_3 used for pH adjustment.

[d]As in Study 2, Procedure *b*.

study findings; the solution in the foam flotation column remained turbid no matter how long foam flotation was carried out. Foam flotation following Procedure *d* was successful if the pH of the nickel solution prior to the addition of LIX65–base is below 8.0. Foam flotation runs made with the pH of the Ni(II) solution above 8.0 prior to the addition of LIX65 following Procedure *d* gave essentially the same results as those resulting from Procedure *c*. Some of the results obtained from Procedure *d* are shown in Table 5. As the data show, nonreproducible results were obtained even when the pH of Ni(II) solution was below 8.0 prior to adding LIX65-base. When NH_3 was used to adjust the pH, the residual Ni(II) concentration was larger than when NaOH was used; we attribute this to the formation of the soluble nickel–ammine complex.

Foam flotation using Procedure *e* at various pH's was effective, and reproducible removal was attained as long as the pH of the Ni(II) solution was below 7.0 before the addition of LIX65. Results are shown in Table 6. The green precipitate was removed with a carrier foam in the same manner as the Cu–LIX65 precipitate. These studies of foam flotation of Ni(II) with LIX65 should be interpreted while keeping in mind that the solubility product of $Ni(OH)_2$ is 6.2×10^{-16} mol^3/L^3. It seems that the Ni–LIX65 complex is not favored over NiOH, unlike the situation with copper. When the Ni–LIX65 complex forms, it cannot be broken by subsequent addition of hydroxide ion, as the results of Table 6 show. Fifty ppm Ni(II) corresponds to a 8.51×10^{-4} *M* solution, so the original solution has a 2.9:1 Ni(II):LIX65 molar ratio. Since all the nickel was in the

TABLE 5

Foam Flotation of Ni(II) with LIX65 Following Procedure *d*[a]

pH before	3.2	3.2	3.2	3.2	3.2	3.2	8.65	8.7	8.65
pH after	9.15[b]	9.2	9.45[b]	9.7	9.92	10.75	9.0	9.0	10
Ni(II) residual (ppm)	>10	3.0	8.0	1.3	0.4	1.5	~10	6.1	0.6

[a] The original solution contained 50 ppm Ni(II) and 100 ppm LIX65. NaOH used to adjust the pH.

[b] NH_3 used to adjust the pH.

TABLE 6

Foam Flotation of Ni(II) with LIX65 Following Procedure *e*[a]

pH before	6.2	6.0	5.2	6.2	6.7	6.6
pH after	8.5	9.0	9.4	9.65	10.0	10.5
Residual Ni(II) (ppm)	>10	0.9	0.15	0.15	0.15	0.1

[a] 50 ppm Ni(II) and 100 ppm LIX65 in original solution. NaOH for pH adjustment. 25 ppm TX100 as carrier surfactant.

TABLE 7

Effect of Ionic Strength and Interfering Anions on Foam Flotation of Ni(II) with LIX65. Procedure *e*[a]

EDTA				PO_4^{3-}				SO_4^{2-}			
Conc (ppm)	pH before	pH after	Residual Ni(II) (ppm)	Conc (ppm)	pH before	pH after	Residual Ni(II) (ppm)	Conc (ppm)	pH before	pH after	Residual Ni(II) (ppm)
25	5.7	10.0	4.65	25	5.6	10.0 (9.6)[b]	0.5	0.025	6.1	10.0	1.2
50	5.7	10.0	11.6	50	5.6	10.0 (9.75)[b]	1.4	0.050	5.2	10.0	0.75
				75	5.6	10.0 (9.50)[b]	0.65	0.10	6.1	10.0	≫10
									5.6	10.0	≫10
								0.2	6.1	10.05	2.8

[a] The original solution contained 50 ppm Ni(II) and 100 ppm LIX65. NaOH used to adjust the pH.

[b] Value in parentheses is foam flotation pH.

TABLE 8

Precipitation Studies of Co(II) with LIX65. Procedure *a*[a]

	Study 1[b]						Study 2[c]					
pH before	8.2	9.0	9.95	11.0	10.15[d]	9.35[d]	8.45	8.95	9.45	10.05	9.35[d]	10.0[d]
pH after	6.2	8.35	9.6	10.85	9.9	8.45	7.9	8.7	9.25	9.7	9.10	9.9
Co(II) in supernatant liquid	≫10	5.0	0.45	0.2	0.33	3.7	≫10	3.7	1.8	1.9	3.2	1.5

[a] The original solution contained 50 ppm Co(II) and 100 ppm LIX65.

[b] NaOH was used to adjust the pH.

[c] NH_3 was used to adjust the pH.

[d] 200 ppm LIX65 was used.

precipitate, the possibility that the NiL_2 or NiL^+ complex is the predominant species is ruled out; it is quite possible to have one or more types of complex, including a bi- or polynuclear complex. Another possibility is the formation of Ni–LIX65 and $Ni(OH)_2$ as a coprecipitate, with the Ni–LIX65 coating the $Ni(OH)_2$ and making it surface-active.

The effects of ionic strength and the presence of anions like phosphate and EDTA on the foam flotation of Ni–LIX65 were studied. Procedure *e* was followed, and the interfering anion was added prior to the addition of LIX65. The results are shown in Table 7. In the presence of sulfate anion good removal was obtained for sulfate concentrations less than 0.1 *M*. In the presence of EDTA the removal was not complete even at an EDTA concentration of only 25 ppm. When phosphate was present, the pH tended to get lower as the stirring went on after adjustment to the required pH, and the foam generated by TX100 was not able to carry the precipitate even if only 50 ppm of phosphate was used. Twenty-five ppm TX100 and 25 ppm HTA were needed to carry the precipitate in the presence of phosphate. Apparently a negatively charged precipitate was formed in the presence of phosphate, so HTA was needed to float the precipitate, although HTA alone was not capable of carrying all the precipitate. Therefore TX100 was used with HTA.

Cobalt(II)

Precipitation studies on the Co(II)–LIX65 system were carried out following Procedure *a*. Dark brown precipitates were formed and a clear supernatant liquid was obtained at pH's above 8.5. Below pH 8.5 turbid solutions with cobalt concentrations of more than 10 ppm were obtained. Results are shown in Table 8. The tabulated data show that LIX65 can precipitate Co(II) effectively, and can displace hydroxide ions as well as ammine ligands. The data also show that the same results are obtained whether 100 or 200 ppm LIX65 was used, and that the results were better when NaOH was used to adjust the pH than when NH_3 was used.

Foam flotation runs at various pH's have been carried out following Procedure *c*. The results are shown in Table 9. Good removal was achieved

TABLE 9

Foam Flotation of Co(II) with LIX65. Procedure *c*[a]

pH before	8.3	8.6	9.05	9.6	10.05	10.5	11.1
pH after	7.55	8.1	8.15	8.6	9.4	10.2	10.9
Residual Co(II) (ppm)	>10	5.0	2.2	0.6	<0.2	<0.1	<0.1

[a] 50 ppm Co(II) and 100 ppm LIX65 in original solution. NaOH was used to adjust the pH. 25 ppm TX100 used as carrier surfactant.

at pH's above 9.0. The sparse foam generated by LIX65 was capable of removing most of the precipitate from solution, and TX100 was used to carry the precipitate away from the liquid in the foam flotation column. The solution was clear after less than a minute of foaming even before the addition of TX100. The molar concentrations and stoichiometry [8.48×10^{-4} *M* in Co(II) and 2.93×10^{-4} *M* in LIX65 in the original mixtures] suggest the formation of a bi- or polynuclear complex between Co(II) and LIX65 in the same manner as with the Cu–LIX65 system.

The effects of ionic strength and interfering anions were studied by carrying out foam flotation runs at pH's around 10.0 in which the anion in question was added to the Co(II) solution prior to pH adjustment and the addition of LIX65. The results are shown in Table 10. When sodium sulfate was added to study interference from sulfate ion and ionic strength, an olive-green precipitate similar to the copper(II)–LIX65 complex color was obtained for Co(II)–LIX65 rather than the usual dark brown precipitate.

Manganese

Precipitation studies following Procedure *a* have been carried out at pH's in the range 9–11. The same results were obtained using 100 and 200 ppm LIX65 with 50 ppm Mn(II); also, the results were the same whether NaOH or NH_3 was used to adjust the pH. The results are shown in Table 11. During the course of vigorous stirring the pH decreased with time, so drops of NaOH or NH_3 solution were added and the pH was monitored. When the pH remained stable for 1.5–2 min (after 25–35 min of vigorous stirring), the stirring was reduced and eventually stopped and the pH measured. The pH in Table 11 referred to as "pH after" refers to the value recorded in this manner and not to the value to which it dropped freely as in the case of the other metal ions studied.

The precipitation studies suggested that foam flotation could profitably be carried out. Foam flotation runs following Procedure *c* at pH 9.5 or lower using TX100 as the carrier surfactant were not successful. Very little foam or no foam at all was produced when 25–35 ppm TX100 was injected three times at 5-min intervals after aeration for 1 min, making the total of TX100 75–105 ppm. On the other hand, at pH's higher than 9.6 a foam was formed which carried the precipitate and left behind a light brown solution containing no visible particles in the foam flotation column. When samples were withdrawn and analyzed using atomic absorption, nonreproducible values in the range 1.5–7.0 ppm residual Mn were obtained. When Procedure *d* was followed, a clear solution with some very small suspended particles was obtained after foam flotation; these particles made the results nonreproducible.

TABLE 10

Effects of Ionic Strength and Interfering Anions on the Foam Flotation of Co(II) with LIX65. Procedure c[a]

SO_4^{2-}				PO_4^{3-}				EDTA			
Conc (*M*)	pH before	pH after	Residual Co(II) (ppm)	Conc (ppm)	pH before	pH after	Residual Co(II) (ppm)	Conc (ppm)	pH before	pH after	Residual Co(II) (ppm)
0.025	10.0	9.6	1.75	25	10.0	9.55	0.6	25	10.0	9.75	4.0
0.05	10.0	9.5	2.6	50	10.0	9.6	2.6	50	10.0	9.4	9.0
0.10	10.0	9.53	3.5	75	10.0	9.65	3.35				
0.20	10.05	9.6	3.45								

[a] 50 ppm Co(II) and 100 ppm LIX65 in original solution. NaOH for pH adjustment. 25 ppm TX100 used.

TABLE 11

Precipitation Studies of Mn(II) with LIX65. Procedure a[a]

pH before	9.0	9.45	9.95	11.0	10.25[b]	9.9[c]
pH after	8.6	8.9	9.75	10.8	10.05	9.7
Mn(II) in supernatant liquid (ppm)	0.33	0.7	1.73	1.46	1.57	0.87

[a] 50 ppm Mn(II) and 100 ppm LIX65 in original solution. NaOH used for pH adjustment.

[b] 200 ppm LIX65 in original solution.

[c] NH_3 used for pH adjustment.

Procedure *e* was then developed for the foam flotation of Mn. The pH was held at 8.0–9.0 during the course of vigorous stirring for 20–35 min. After this period the pH did not decrease at the same rate as it did during the course of stirring. When the pH had been stable for 1.5–2.0 min, the stirring was reduced and then stopped after about 10 min. A brown precipitate with a clear supernatant liquid was obtained. Twenty-five ppm HTA was used to carry the precipitate away from solution in the foam flotation column. The solution became clear upon 5 min or less of foam flotation. The results are shown in Table 12. When NH_3 was used to adjust the pH, it took about 7 min of flotation to remove the precipitate, after which samples were withdrawn.

Procedure *e* was followed for the study of the effect of sulfate and phosphate anions. Twenty minutes of foaming was required when sulfate was used, whereas 15 min of foaming was required in the presence of phosphate. The phosphate or sulfate was added prior to the addition of LIX65. The results are shown in Table 13. Better removal was observed in the presence of phosphate than in the presence of sulfate.

The color of the Mn precipitate formed with LIX65 is dark brown, resembling hydrous MnO_2. This and the observed pH changes suggest that the dark precipitate is MnO_2 which forms according to the equation $2Mn^{2+} + 4OH^- + O_2 \rightarrow 2MnO_2 + 2H_2O$, or Mn_2O_3, which is brown in color also, and not a complex of Mn(II) with LIX65. Two foam flotation runs at pH's 9.3 and 10.5 were carried out with no LIX65 added to the solution mixture as follows: Mn(II) (50 ppm) was stirred vigorously while adjusting the pH to the desired value with NaOH solution. The pH was monitored during the course of vigorous stirring for 20 min, then the stirring was reduced and stopped over a period of 10 min. The solution mixture was transferred to the foam flotation column, aerated for about 2 min, and 25 ppm HTA was then injected into the solution. Another 25 ppm portion of HTA was injected after 5 min of foaming. A foam formed and carried the precipitate out of the solution. For the run at pH 10.5 the solution became almost clear within 18 min of foaming, whereas in the run at pH 9.3 the solution did not become clear even after 35 min of foaming. Samples were taken after 15 min, acidified, and analyzed for Mn by atomic absorption for each of the runs. The analysis showed a residual Mn concentration of 1.0 ppm for the run at pH 10.5 and more than 10 ppm for the run at pH 9.3. MnO_2 does not dissolve in organic solvents such as acetone, ether, and hexane, whereas the precipitate formed in the presence of LIX65 gave a brown solution in the above solvents. The two foam flotation runs and solubility tests indicate that LIX65 is in fact involved in the precipitate obtained from Mn–LIX65 solution mixtures and that these precipitates are not totally MnO_2 or Mn_2O_3

TABLE 12

Foam Flotation of Mn(II) with LIX65. Procedure *e*[a]

	Study 1[b]									Study 2[c]		
Foam flotation pH	7.4	8.0[d]	8.35	8.5	8.5[e]	9.05	9.25	9.4	9.5	10.2	8.9	9.5
Residual Mn(II) (ppm)	>16	3.5	0.5	0.5	0.55	0.6	0.5	0.75	1.35	3.9	1.4	1.35

[a] 50 ppm Mn(II) and 100 ppm LIX65 in original solution.
[b] NaOH for pH adjustment.
[c] NH_3 for pH adjustment.
[d] 50 ppm HTA.
[e] 200 ppm LIX65.

TABLE 13

Effect of Sulfate and Phosphate on Foam Flotation of Mn with LIX65[a]

SO_4^{2-}			PO_4^{3-}		
Conc (*M*)	Foamation pH	Residual Mn (ppm)	Conc (ppm)	Foamation pH	Residual Mn (ppm)
0.025	8.15	5.3	25	8.5	1.9
0.05	9.05	2.3	50	8.8	1.75
0.10	8.95	4.5	50	9.0[b]	0.65
			75	8.8[b]	0.45
				8.6	2.0

[a] 50 ppm Mn(II) and 100 ppm LIX65 in original solution. NaOH used for pH adjustment. 50 ppm HTA was used.
[b] 25 ppm HTA used.

although there is strong indication that some manganese oxide or hydroxide is coprecipitated with the Mn–LIX65 precipitate. This is suggested by the requirement for a positively charged carrier surfactant, HTA.

Zinc(II) and Cadmium(II)

Precipitation studies of these metal ions with LIX65 following Procedures *a* and *b* gave some precipitate which looked like the hydroxides. One foam flotation run with Zn(II) following Procedure *c* proved fruitless since most of the precipitate remained in suspension and was not carried out by TX100 or HTA foams.

STUDIES WITH LIX63

LIX63 did not produce a foam when it was introduced to the foam flotation column containing distilled water at various pH's. A carrier surfactant was needed to carry the solid particles away from the solution in subsequent foam flotation runs.

Copper(II)

Precipitation studies following Procedure *a* gave a green precipitate and clear supernatant liquid; NaOH and NH_3 solutions were used to adjust the pH. The results are shown in Table 14. Foam flotation runs at various pH's were carried out following Procedure *c*. The results are shown in Table 15. At a pH of 6.0 or below a green solution was obtained; no precipitate formed after the solution mixture had been left standing for 24 h. Good removal is attained at pH's of 8.0 or above. The same arguments mentioned in the LIX65 studies concerning the possibility of bi- or polynuclear complexes being formed apply here since the molarities of Cu(II) and LIX63 are 7.87×10^{-4} *M* and 3.69×10^{-4} *M*, respectively. The green color predominates here much more quickly than it does in the case of Cu–LIX65, which is attributed to a faster reaction.

The effects of ionic strength and interfering ions were studied using sulfate, phosphate, and EDTA; the anions were added to the Cu(II) solution prior to pH adjustment and the addition of LIX63. The results are shown in Table 16. The solutions were foamed for 20–25 min, and 50 ppm TX100 was needed to carry the solid particles from the solution. In the presence of phosphate, green solutions were left after the foam removed the solid particles. The solutions have a more intense green color in the foam flotation column as the amount of phosphate is increased from 25 to 50 to 75 ppm.

TABLE 14

Precipitation of Cu(II) with LIX63. Procedure *a*[a]

	Study 1[b]						Study 2[c]				
pH before	6.0	7.2	8.2	9.3	10.1	11.0	7.25	8.4	8.9	10.0	10.95
pH after	4.0	7.0	6.75	7.85	9.75	10.95	6.75	8.25	8.8	9.9	10.85
Cu(II) in supernatant liquid (ppm)	≫10	0.65	0.85	0.25	0.3	0.85	1.7	1.2	1.0	0.55	>10

[a] 50 ppm Cu(II) and 100 ppm LIX63.
[b] NaOH used to adjust pH.
[c] NH_3 used to adjust pH.

TABLE 15

Foam Flotation of Cu(II) with LIX63. Procedure *c*[a]

pH before	6.7	7.7	8.0	8.75	9.55	10.0	10.35
pH after	6.0	5.7	6.7	6.6	8.2	9.7	10.1
Residual Cu(II) (ppm)	8.9	3.2	0.85	0.87	0.2	0.2	<0.1

[a] 50 ppm Cu(II) and 100 ppm LIX63 in original solution. NaOH used to adjust the pH. 25 ppm TX100 used as carrier surfactant.

TABLE 16

Effect of Sulfate, Phosphate, and EDTA on Foam Flotation of Cu(II) with LIX63. Procedure c^a

SO_4^{2-}				PO_4^{3-}				EDTA			
Conc (*M*)	pH before	pH after	Residual Cu (ppm)	Conc (ppm)	pH before	pH after	Residual Cu (ppm)	Conc (ppm)	pH before	pH after	Residual Cu (ppm)
0.025	9.0	6.4	2.0	25	10.0	9.85	1.85	25	9.95	9.3	5.0
0.05	9.9	8.4	1.7	50	10.0	9.4	>10	50	9.95	9.5	10.5
0.1	9.95	8.95	1.7	75	9.95	9.6	$\gg10$				

[a] 50 ppm Cu(II) and 100 ppm LIX63 in original solution. NaOH used for pH adjustment. 50 ppm TX100 was used.

TABLE 17

Foam Flotation of Co(II) with LIX63. Procedure c^a

pH before	8.05	8.5	9.2	9.5	10.0	10.5	11.0
pH after	7.5	7.6	8.4	8.4	9.85	9.8	10.4
Residual Co(II) (ppm)	$\gg15$	>10	2.43	2.43	0.2	0.2	<0.2

[a] 50 ppm Co(II) and 100 ppm LIX63 in original solution. NaOH used for pH adjustment.

Cobalt(II)

Precipitation studies following Procedure *a* were carried out at pH 9.5 and 10.15. A light brown precipitate and a clear supernatant liquid formed. Atomic absorption analysis showed residual Co(II) concentrations of less than 1.0 ppm. Foam flotation runs following Procedure *c* were carried out; 50 ppm TX100 was needed to carry the solid particles away from the solution. Twenty-five ppm TX100 was injected at 5 min intervals and foaming was carried out for 20 min. The solution became clear in about 10 min. The results are shown in Table 17. Good removal was obtained at pH's 9.5 or above. Interferences from sulfate, phosphate, and EDTA were studied at a pH of around 10. A brown precipitate was formed in the presence of EDTA and phosphate. This precipitate was not carried away by TX100 even when 75–100 ppm of the surfactant was used. In the presence of sulfate (0.025–0.1 *M*) a green precipitate formed which was not floated by TX100. Attempts to foam float using HTA or HTA–TX100 mixed surfactant proved fruitless.

Nickel(II)

Precipitation studies following Procedures *a* and *b* gave small amounts of orange precipitate. The analysis of the supernatant liquid showed a nickel content of more than 10 ppm in the pH range 8.25–10.7; no precipitate formed at pH's lower than 8.0. Foam flotation studies following Procedure *e* using 100 and 200 ppm LIX63 gave a precipitate and turbid solution; the precipitate was not carried away by TX100, HTA, or mixed surfactant (TX100–HTA). When a solution containing 50 ppm Ni(II) and 300 ppm LIX63 was prepared and foamed, a brownish-yellow precipitate formed which is more voluminous than that which formed when 100 or 200 ppm LIX63 was used. The precipitate was not floated by TX100, HTA, or mixtures of the two.

Manganese(II)

Precipitation studies following Procedure *a* at pH's of 9.5 and 10.4 showed residual manganese levels of 0.5 and 1.85 ppm in the supernatant, respectively. Foam flotation studies following Procedure *e* were carried out. A brown precipitate and a clear supernatant liquid were obtained. This precipitate was not removed completely by TX100, HTA, or TX100–HTA mixtures even if the flotation was carried for 30–40 min and with 75 ppm carrier surfactant.

Zinc(II) and Cadmium(II)

Precipitation studies indicated that these two metal ions cannot be precipitated effectively with 100 or 200 ppm LIX63. No foam flotation studies were done with them.

CONCLUSIONS

Good removal of Cu(II) was possible with LIX65 at pH's higher than 7.5 in the presence of ammonia and also when the pH was adjusted with sodium hydroxide. LIX65 was capable of removing Cu(II) in the presence of sulfate, phosphate, and EDTA. For Ni(II) and Co(II) the removal was very good at pH's of 9.0 or above and in the presence of sulfate and phosphate. For Mn(II) the removal was good in the pH range of 8.3–9.5, although maintaining an elevated pH while stirring vigorously was necessary. Removal of Mn in the presence of phosphate was good at pH's around 9.0.

If the studies with LIX65 are compared with studies with NLS and $Fe(OH)_3$ (*19*), it can be concluded that LIX65 is less subject to interferences. The economics of NLS and $Fe(OH)_3$ compared to LIX65 certainly favor the former if we consider only batch processes in which no recycling of LIX65 is carried out. Generally, in the extraction of metal ions with LIX65 reagents, the recovery and the reuse of LIX is a fundamental step, and this can be done by breaking the metal–LIX complex with acids. Collection of the foamate, acidification, and extraction with an organic solvent would presumably permit recovery of LIX65 for recycle.

Our studies show that LIX63 is not nearly as effective as LIX65. Good removals of copper and cobalt were found, but removals of nickel and manganese were poor. The ability of LIX63 to remove copper and cobalt is impaired by the presence of phosphate, EDTA, and even excess sulfate (in the case of cobalt).

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