Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Bita R. Fillipi[a]; John F. Scamehorn[a]; Richard W. Taylor[a]; Sherril D. Christian[a]
[a] INSTITUTE FOR APPLIED SURFACTANT RESEARCH UNIVERSITY OF OKLAHOMA NORMAN, OKLAHOMA, USA

To cite this Article Fillipi, Bita R. , Scamehorn, John F. , Taylor, Richard W. and Christian, Sherril D.(1997) 'Selective Removal of Copper from an Aqueous Solution Using Ligand-Modified Micellar-Enhanced Ultrafiltration Using an Alkyl-β-diketone Ligand', Separation Science and Technology, 32: 15, 2401 — 2424

To link to this Article: DOI: 10.1080/01496399708000777

URL: http://dx.doi.org/10.1080/01496399708000777

SEPARATION SCIENCE AND TECHNOLOGY, **32**(15), pp. 2401–2424, 1997

Selective Removal of Copper from an Aqueous Solution Using Ligand-Modified Micellar-Enhanced Ultrafiltration Using an Alkyl-β-diketone Ligand

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BITA R. FILLIPI, JOHN F. SCAMEHORN,*
RICHARD W. TAYLOR, and SHERRIL D. CHRISTIAN
INSTITUTE FOR APPLIED SURFACTANT RESEARCH
UNIVERSITY OF OKLAHOMA
NORMAN, OKLAHOMA 73019, USA

ABSTRACT

The semiequilibrium dialysis technique has been used to investigate the concentration of Cu^{2+} using a water-insoluble liquid ion exchanger or ligand with cationic surfactant in a ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) process. In LM-MEUF the surfactant and the ligand are added to an aqueous solution containing ions of like charge, one of which needs to be selectively removed. The ligand forms a complex with the target ion of interest and solubilizes or dissolves inside the organic interior of the micelles. Therefore, it is possible to replace typical solvent extraction solvents such as kerosene by micelles. In this study copper chloride/calcium chloride solutions were treated for the extraction of copper using a commercially available ligand, 1-phenyl-3-isoheptyl-1,3-propane dione in cetyltrimethylammonium bromide (CTAB), a cationic surfactant. The effect of pH and the concentrations of copper, calcium, surfactant, and ligand on the efficiency of copper removal from water are discussed. Copper rejections greater than 99% were obtained even in the presence of calcium. In studies of regeneration of surfactant and ligand from the retentate stream containing rejected species, stripping of copper from the retentate was achieved using sulfuric acid. Stripping efficiencies greater than 94% were attained in three to four stages, demonstrating the feasibility of this regeneration scheme.

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* To whom correspondence should be addressed.

INTRODUCTION

Surfactant-based separation processes have great potential in large-scale industrial applications for removal and/or recovery of organic pollutants and heavy metals from wastewater streams (1). Surfactant-based separation processes can be less expensive, require less energy, and be environmentally safer compared to traditional separation techniques such as distillation or liquid–liquid extraction (1).

In traditional solvent extraction processes, a metal such as copper is often selectively extracted from a dilute, impure leach solution into an organic liquid. The copper ions are then stripped with sulfuric acid from the organic liquid into a concentrated, purified electrolyte solution suitable for electrowinning. The organic phase consists of a chemically active component and an organic solvent. The active reagent (ligand) dissolves readily in the organic solvent and extracts copper from the dilute leach solution (aqueous phase) into the organic phase. The transfer of copper ions from the aqueous to the organic phase (extraction) and from the organic to aqueous phase (stripping) is a reversible reaction and is controlled by adjusting the pH of the aqueous phase (2). A schematic diagram of a typical copper extraction plant is shown in Fig. 1. Kerosene is a common organic solvent in copper extraction operations. There are a number of problems associated with the use of kerosene; e.g., furnishing adequate fire-fighting equipment, providing a facility for preventing accidental discharge to streams or rivers, high capital cost of the organic inventory of the plant, removal of residual kerosene from streams leaving the plant, and health hazards related to the use of kerosene (3). Because of the environmental concerns associated with the use of such solvents, it is highly desirable to develop an economically attractive, surfactant-based separation technique to selectively remove heavy metal ions from wastewater streams. Until recently, a common disadvantage of the surfactant-based methods has been their lack of selectivity for a target species in the presence of similar species that are often present in large excess. For example, if the target species is a metal cation, other cations may also bind to the surfactant and consequently reduce the binding capacity and separation efficiency for the target ion.

To enhance selectivity in separation, we have developed a novel surfactant-based separation technique, namely ligand-modified micellar-enhanced ultrafiltration (LM-MEUF), in our laboratories (4–9). This technique involves addition of a ligand to the ultrafiltration system where the ligand has both a high solubility in the micelles and a tendency to complex the target metal ion selectively. Micellar extraction of metal ions using an ultrafiltration technique has also been reported by Tondre and coworkers

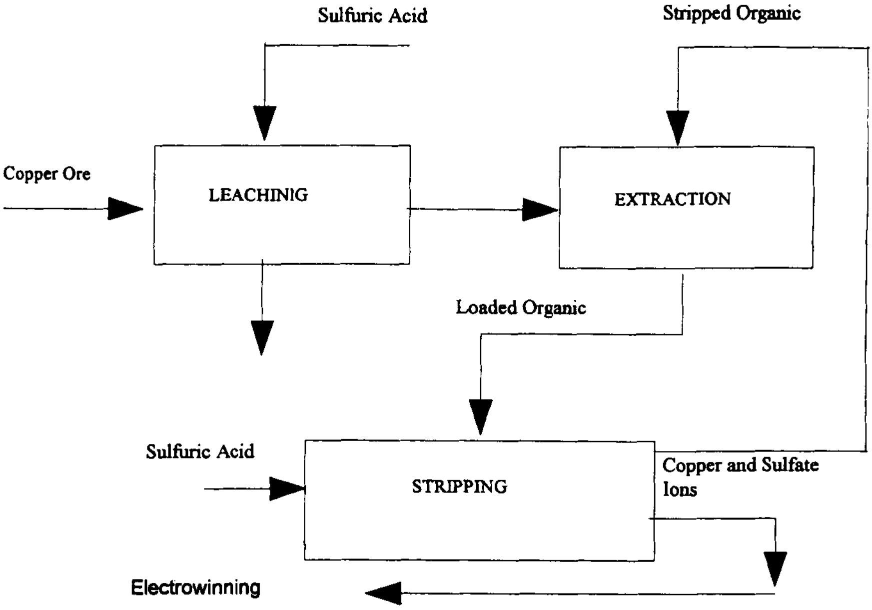

FIG. 1 Schematic of traditional copper extraction process.

including studies on ligand–metal complexation and kinetically controlled separation of metal ions (10–13).

This paper describes the use of the cationic surfactant cetyltrimethylammonium bromide (CTAB) and a commercially available ligand for selective removal of Cu^{2+} from a Cu^{2+}/Ca^{2+} solution. The reason for using Ca^{2+} as the competing cation in the solution is to demonstrate the effectiveness of the LM-MEUF process for selective removal of a model target metal cation (e.g., Cu^{2+}) which can either have value or be a toxic pollutant in the presence of a nontoxic and valueless ion of the same charge that does not need to be removed. In addition, regeneration schemes for the recovery of the surfactant and the ligand downstream of the ultrafiltration are outlined.

BACKGROUND

Micellar-enhanced ultrafiltration (MEUF) is a surfactant-based separation technique which can be used to remove metal ions and/or dissolved organics from aqueous streams. Metal ions bind to the surface of negatively charged micelles of an anionic surfactant while organic solutes tend to dissolve within the micelles (14–22, 28, 32). A disadvantage of MEUF in removing dissolved metals from aqueous solutions is that there is very little selectivity except on the basis of charge. For example, Ca^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} are removed nearly to the same extent in MEUF, using an anionic surfactant (16, 21).

Ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) is a modification of MEUF which is designed to introduce selectivity in the removal of cations (4–9). In LM-MEUF a surfactant and a ligand are added to the contaminated solution. The surfactant is present at a concentration well above its critical micelle concentration (CMC), so most of the surfactant is present as micelles. The micelles are roughly spherical aggregates containing about 50 to 150 surfactant molecules (23). The hydrocarbon chains of the surfactant occupy the micelle interior, making this core hydrophobic, and the hydrophilic portions of the surfactant are situated at the micelle surface. A suitable ligand for LM-MEUF needs to have a hydrophilic moiety which can selectively complex the target metal ion. Furthermore, to minimize the loss of the amphiphilic ligand during the separation process, the ligand–metal complex should have a large solubilization constant in the micelles and hence a large hydrophobic moiety. Therefore, the ligands used in LM-MEUF need to have the same general characteristics as the ligands used in solvent extraction for selective metal removal (24, 25). Once the ligand selectively complexes with the target ion of interest, that ion will also become associated with the micelles through this ligand solubilization phenomenon. This solution containing surfactant/ligand/ion is then treated by an ultrafiltration process with membrane pore sizes small enough to reject or block the micelles. As micelles are rejected, the solubilized ligand and its associated ions will also be rejected. The unsolubilized ligand, uncomplexed ions, and surfactant monomers pass through the ultrafiltration membrane to the permeate side (4–9).

A retentate-based rejection (in %) is defined as:

$$\text{Rejection} = (100)(1 - [\text{solute in permeate}]/[\text{solute in retentate}]) \tag{1}$$

The resulting permeate stream from LM-MEUF contains very low concentrations of the surfactant, target metal, and the ligand, and hence high rejection values for each of these species. By using a cationic surfactant in the LM-MEUF process, it is possible to expel the cations that are not specifically bound to the solubilized ligand into the permeate by a process called ion-expulsion ultrafiltration (IEUF) (22, 26, 27). A Donnan-equilibrium effect causes the uncomplexed cations to become concentrated in the permeate; in this way, extremely large selectivities can be achieved with LM-MEUF (4, 7, 8). Consequently, a dilute process stream with a fairly large volume can be separated into a small concentrated retentate stream containing a large percentage of the surfactant/ligand/target ion, and a large volume of permeate that contains toxins in low concentrations. Staging the ultrafiltration units (17) can permit the ultimate permeate to have any desired degree of purity so it can be discarded or reused. The retentate stream is considerably smaller in volume than the original process stream, and therefore further treatment or disposal of this retentate can be less expensive than treatment of the original process stream. The monomer (surfactant molecules not in micellar form) in the retentate is not significantly rejected by the ultrafiltration membrane. Therefore, the surfactant concentration in the permeate is approximately equal to the monomeric surfactant concentration in the retentate or the surfactant critical micelle concentration (CMC) (15, 28). Incorporation of amphiphiles with hydrophilic and hydrophobic groups, such as a ligand into an ionic micelle where the ligand hydrophilic group is neutral or has a charge opposite to that of surfactant, tends to cause separation of the charged surfactant hydrophilic head groups, reducing electrical repulsion in the Stern layer of the micelles (29–34). As the micellar charge density and the absolute value of the electrical potential at the micellar surface are reduced, less work is required to insert an ionic surfactant into the micelle due to reduced electrical repulsion. The resulting CMC is lower than the CMC of the pure surfactant, which causes an increase in micellar concentration and consequently an improved separation efficiency, as well as lower loss levels of surfactant in the permeate.

In previous LM-MEUF studies, selective removal of Cu^{2+} from a Cu^{2+}/Ca^{2+} solution has been accomplished using the ligand *N*-*n*-(dodecyl)-iminodiacetic acid (NIDA) with the cationic surfactant *N*-hexadecylpyridinium chloride (CPC). Rejections of Cu^{2+} of greater than 99% were reported with no rejection of Ca^{2+} (4, 5). Comparable rejections of Cu^{2+} have been observed using the ligand 4-hexadecyloxybenzyliminodiacetic acid (BIDA) in CPC in the presence of Ca^{2+} with once again no rejection of Ca^{2+} (7). The surfactant and ligand need to be recovered from the retentate for reuse for an economical operation. In this study we will discuss a recovery/regeneration process for the surfactant and the ligand from the retentate stream and several disposal options for the target metal.

The semiequilibrium dialysis (SED) technique, which has been developed in our laboratory, is a simple experimental method for investigating both solubilization of organic species in surfactant micelles and the binding or expulsion of ions by micelles. Since MEUF processes are equilibrium-controlled rather than kinetically-controlled, the results of simple SED experiments can be used to predict the effectiveness of ultrafiltration (UF) purification processes for rejected species (5, 6, 8, 9, 19, 22, 35–40). In this study the SED results are used to determine the rejection of Cu^{2+} in the LM-MEUF process. The ion expulsion of uncomplexed Ca^{2+} measured by SED will accurately reflect equilibrium compositions, but will not generally agree quantitatively with ultrafiltration results (26, 27).

In our past work on LM-MEUF, we have synthesized the ligands used (4–9). One unique aspect of the present study is the use of a commercially available ligand, an important factor in facilitating the ultimate industrial application of the technology. Figure 2 is an integrated process flow diagram for the LM-MEUF process incorporating the stripping regeneration step.

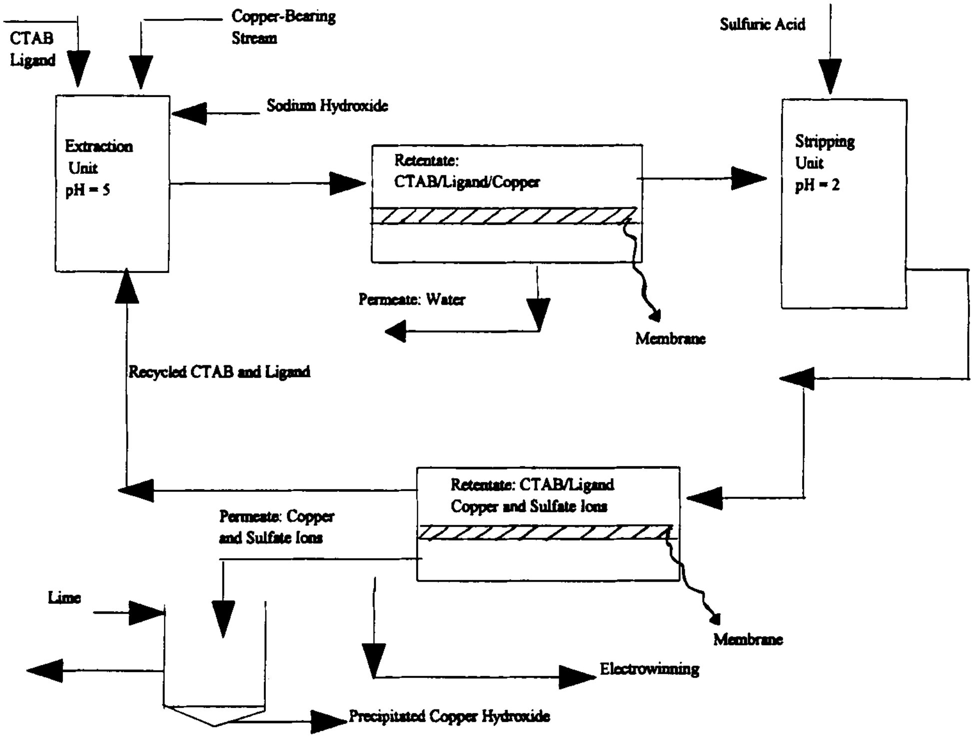

FIG. 2 Schematic of LM-MEUF copper extraction process.

EXPERIMENTAL

Materials

The cationic surfactant, cetyltrimethylammonium bromide (CTAB, 99% purity), was purchased from Sigma. The liquid ion exchanger used was a commercial product known as Lix54, a beta-diketone ligand, from Henkel Corp.; it is 1-phenyl-3-isoheptyl-1,3-propane dione and its structure is shown in Fig. 3. The ligand is designed to extract copper from ammoniacal leach solutions (24, 41). The surfactant and ligand were used as received.

The regenerated cellulose membranes (6000 Da molecular weight cutoff) were purchased from Fisher Corp. Fisher Certified ACS grade $CuCl_2 \cdot 2H_2O$ and $CaCl_2 \cdot 2H_2O$ were used as the source of copper and calcium ions. Copper chloride dihydrate and calcium chloride dihydrate are hygroscopic; they were dried in an oven at 240°C for 24 hours prior to use. The sodium hydroxide and the sulfuric acid used in all experiments were analytical reagent grade from Fisher Chemical Co. The water was treated by carbon adsorption and double ion exchange.

Methods

All experiments were carried out at 30°C. Semiequilibrium dialysis experiments were carried out as described previously (5, 6, 8, 9, 19, 22, 35–40). The cell is made of two acrylic blocks with concave compartments. One chamber was filled with the surfactant/ligand/copper solution (retentate side), and the other chamber was filled with water (permeate side). The membranes were soaked in double deionized water for 24 hours before being used. The membrane pore sizes were sufficiently small to block the passage of micelles, so the permeate contained only the surfactant monomers, unsolubilized ligand, and uncomplexed metal. The equilibration period was 22 to 24 hours, at which time the samples were removed from the chambers on each side of the membrane. If the solution is allowed to equilibrate for extremely long times, a significant concentration of mi-

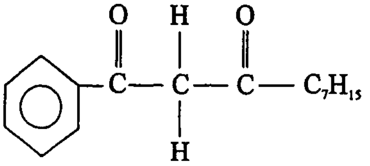

FIG. 3 Schematic of the ligand structure.

celles can occur in the permeate, but over a 24-hour time period, the surfactant monomer, uncomplexed metal, and unsolubilized ligand are at nearly the same activity (for ions, each ion-pair is at the same activity) in retentate and permeate.

A Varian AA-20 variable wavelength atomic absorption spectrophotometer was used to measure the concentration of Cu^{2+} and Ca^{2+} in the permeate and retentate (after semiequilibrium was reached) in order to determine the rejection of these ions. A Bausch & Lomb Spectronic 1001 variable wavelength UV absorption spectrophotometer (wavelength 260 nm) was used to determine the ligand concentration in the retentate and permeate samples. The CTAB concentrations in permeate samples were determined using a Perkin-Elmer Liquid Chromatograph with an Alltech-320 Conductivity Detector and a Varian 4270 Integrator. The pH measurements were made on a Fisher Accumet Model 420 Digital pH/Ion Meter using a Fisher Standard Glass Body Combination Electrode. All solutions were adjusted to the desired pH using sodium hydroxide and sulfuric acid. To determine protonation and metal–ligand stability constants, potentiometric titrations were performed with an Orion EA 940 expandable ion analyzer, with an Orion Research, Sure-Flow Ross Combination pH electrode as described previously (5, 6, 8, 9).

The SED method was also used for the stripping (regeneration of surfactant/ligand) portion of this study. The stripping of Cu^{2+} from the ligand was accomplished with the use of sulfuric acid at a pH of about 2.0. To achieve the desired degree of separation, stripping experiments were staged; i.e., the permeate from the first SED cell (after semiequilibrium is reached) becomes the feed or the retentate to the second stripping stage (second SED cell) and so on. To make up for solution losses, multiple SED cells at identical concentrations were made for each stage. After semiequilibrium was reached, the retentate copper contents of identical cells were analyzed; if there was less than a 5% difference in copper concentrations, the retentates were combined and once again the copper content of this solution was measured. The resulting retentate became feed to the next SED stage.

RESULTS AND DISCUSSION

Ligand Protonation and Metal Complexation Constants

The commercial ligand chosen is designed to form strong complexes with Cu^{2+} in ammoniacal leach solutions (24, 41). This ligand is highly insoluble in water in the absence of the surfactant. Cationic surfactants are preferred in this application of LM-MEUF because they expel other cations to the permeate due to the ion expulsion effect (4, 5, 7, 26, 27).

Therefore, great selectivity can be achieved if the formation constant of the metal–ligand complex is large enough to overcome the charge repulsion between the positively charged target metal ion and the positively charged micelle (4–9).

Complexation of the ligand with metal ions requires relatively high values of the effective complex formation constant, K_{ML}, where ML denotes the metal–ligand complex. For example, to reduce the free metal ion concentration to 1%, the value of the K_{ML} must be at least 1×10^7 M^{-1} (assuming that the initial concentrations of the ligand and the metal ion are 1 mM). For a mixture of the ligand and two cations (each initially at 1 mM), the target cation (M) must have a complexation constant of at least 10^6 times larger than that of the other cation (M*) so the concentration of the metal–ligand complex in the solution is greater or equal to 99% of the total concentration of the target cation ($[M]_{total}$) in the solution; $[ML] \geq 0.99[M]_{total}$ (6, 8, 9, 24, 25).

For a ligand with low solubility in water, the values of ligand protonation and metal:ligand equilibrium constants can be determined from the values obtained for the chelating portion of the ligand which is usually soluble in water (6, 9). Protonation and metal–ligand formation constants are available for most commonly used chelating groups and can be used to calculate these constants (24, 25, 42). However, replacing the organic solvent with a micellar solution can result in changes in ligand protonation and ligand:metal complexation equilibria. Previous results (9) suggest that the conformational freedom of the ligand in micelles becomes limited, causing alterations in metal: ligand complexation behavior.

Protonation and complexation equilibria pertinent to this investigation are given by Eqs. (2)–(5).

Protonation of ligand:

$$HL \rightleftharpoons L^- + H^+ \tag{2}$$

$$K_a = [L^-][H^+]/[HL] \tag{3}$$

Metal–ligand complexation:

$$\beta_1 = [ML^+]/[M^{2+}][L^-] \tag{4}$$

$$\beta_2 = [ML_2]/[M^{2+}][L^-]^2 \tag{5}$$

K_a represents the stepwise acid dissociation constant. Complex formation constants can be expressed as either stepwise constants, K_{ML}, or cumulative formation constants, β (6, 8, 24, 25, 42).

A solution containing 3 mM ligand in 0.03 M CTAB was titrated with a 0.1 M NaOH solution. Figure 4 shows plots of the observed pH as a function of volume of NaOH added in these experiments. The titration

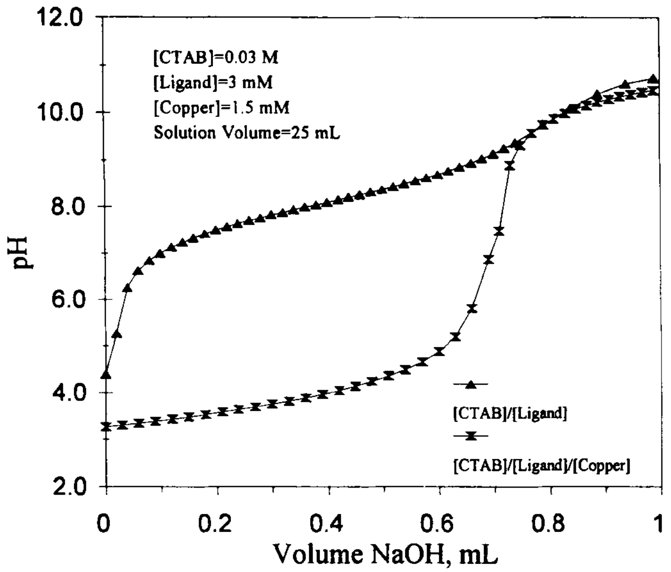

FIG. 4 Titration results for CTAB/ligand/copper with 0.1 M NaOH.

data are fitted using computer programs PKAS (43) to determine a K_a of $10^{-8.06}$ (pK_a of 8.06). Figure 4 also includes data for titration of a solution of 1.5 mM Cu^{2+}, 3 mM ligand, and 0.03 M CTAB with 0.1 M NaOH. Computer program BEST (44) was used to calculate ligand–metal complex formation constants from these data; $\beta_1 = 10^{6.79}$ and $\beta_2 = 10^{14.02}$. Equations (4) and (5) have specific relevance to the determination of the stoichiometric ratios of ligand to Cu^{2+}. A ligand to Cu^{2+} stoichiometric ratio of 2 to 1 was used to calculate β_1 and β_2. The calculated values compare well to literature values for the same chelating group (42).

The titration data show that ligand:Cu^{2+} complexes start to form at a pH of approximately 4, and the end point is reached at a pH of about 7, indicating that this ligand displays similar protonation characteristics in CTAB as it does in kerosene (41).

Ultrafiltration Separation Efficiency

The SED experiments were carried out at feed (initial retentate) CTAB concentrations of 0.01 and 0.03 M and at a pH of 3 or 5 with varying ligand, copper, and calcium concentrations; the results are presented in Tables 1–3 and Figs. 5–15. The data are plotted as rejections to illustrate

TABLE 1
Copper Rejection in 0.01 M CTAB (Feed)

pH	Feed [ligand] (mM)	Retentate [copper] (mM)	Permeate [copper] (mM)	Rejection (%)
3.5	1	0.095	0.0259	72.9
	1	0.228	0.130	42.98
	1	0.456	0.322	29.38
	1	1.007	0.834	13.30
	1	2.754	2.754	—
5.5	1	0.126	0.005	96.12
	1	0.197	0.107	45.70
	1	0.433	0.275	36.49
	1	0.834	0.716	14.15
	1	2.675	2.675	—
3.5	3	0.137	0.00189	98.62
	3	0.307	0.0496	83.84
	3	0.504	0.208	58.73
	3	0.928	0.692	25.43
	3	2.675	2.408	9.98
5.5	3	0.113	0.000189	99.83
	3	0.246	0.000157	99.93
	3	0.504	0.0002	99.96
	3	0.669	0.197	70.55
	3	1.503	1.062	29.32
3.5	6	0.152	0.0111	92.7
	6	0.315	0.075	76.0
	6	0.386	0.26	32.6
	6	0.826	0.606	26.6
5.5	6	0.1802	0.00008	99.96
	6	0.354	0.00007	99.98
	6	0.677	0.00008	99.99
	6	1.377	0.0002	97.66

the effectiveness of the separation, and as permeate copper concentrations to illustrate data when rejections are high and trends in rejections are difficult to observe. Figure 5 is plot of permeate [copper] as a function of retentate [copper]. This plot shows that the permeate copper concentration increases with an increase in retentate copper concentration, while the permeate copper concentration decreases with increasing feed (initial retentate) ligand concentration. This trend is expected because the ligand molecules complex with unbound Cu^{2+} in the solution and solubilize in-

TABLE 2
Copper Rejection in 0.03 M CTAB (Feed)

pH	Feed [ligand] (mM)	Retentate [copper] (mM)	Permeate [copper] (mM)	Rejection (%)
5.5	1	0.13	0.0001	99.91
	1	0.259	0.0282	89.11
	1	0.37	0.236	36.22
	1	0.641	0.57	89.8
	1	2.43	1.722	—
	3	0.213	0.000275	99.87
	3	0.431	0.000267	99.94
	3	0.835	0.000535	99.93
	3	1.099	0.2832	74.23
	3	2.353	1.841	21.75
	6	0.199	0.00118	99.41
	6	0.404	0.00055	99.86
	6	0.752	0.00055	99.93
	6	1.394	0.00079	99.94
	6	1.22	2.801	56.44

side the micelles. The micelles and their associated ligand:metal complexes are retained on the retentate side of the membrane of UF, consequently improving copper rejection efficiency. At 1.5 mM retentate copper concentration, the increase in feed ligand concentration from 1 to 6 mM causes an approximately 700-fold reduction in permeate copper concentration, indicating the large influence of this variable.

Figure 6 shows that at constant feed ligand concentration, increasing the pH causes a moderate increase in copper rejection. However, at a

TABLE 3
Copper Rejection in the Presence of Calcium: Feed [CTAB] = 0.03 M, Feed [ligand] = 3 mM, Feed [copper] = 0.7 mM

Feed	Retentate (mM)		Permeate (mM)		Copper
[calcium] (mM)	[Copper]	[Calcium]	[Copper]	[Calcium]	rejection (%)
0.293	0.683	0.123	0.00009	0.184	99.99
0.642	0.646	0.206	0.00007	0.384	99.99
1.31	0.667	0.318	0.00016	0.617	99.97
2.42	0.727	0.951	0.00019	1.057	99.97
6.81	0.670	2.207	0.00013	3.256	99.98

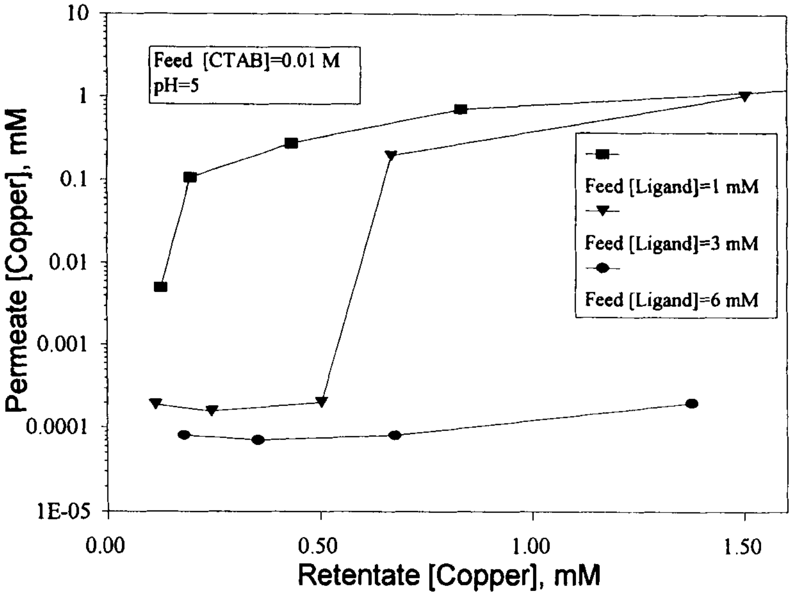

FIG. 5 Permeate copper concentration as a function of retentate copper concentration with varying ligand concentration.

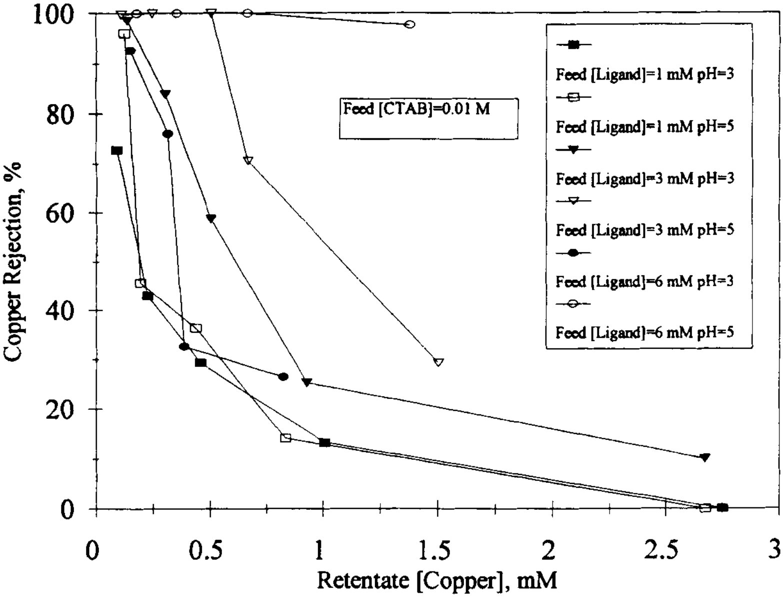

FIG. 6 Copper rejection as a function of retentate copper concentration with varying pH and ligand concentration.

feed pH of 5, increasing the feed ligand concentration results in a significant increase in copper rejection. As shown in Fig. 6, at a retentate copper concentration of 1.5 mM, an increase in feed ligand concentration from 1 to 6 mM results in improved copper rejection values from 10% to approximately 99%.

At low retentate copper concentration or high feed ligand/copper concentration ratio, almost quantitative removal is attained (rejection exceeds 99%). This condition is maintained until a higher retentate copper concentration or a lower feed ligand/copper concentration ratio at higher feed surfactant concentrations is approached. The CMC of CTAB is less than 0.001 M under conditions used here while the feed surfactant concentrations are at least an order of magnitude above the CMC. The CMC of a surfactant is the concentration at which micelles start to form (23). Once the CMC is reached, the monomeric surfactant concentration remains approximately constant; any increase in the concentration of the surfactant results in formation of additional micelles. Since ligand:metal complexes dissolve inside the micelles, increasing micellar concentration should improve copper rejection values as observed here. Under the conditions shown in Figs. 7–9, it is critical to design a system where the feed ligand/copper molar ratio is above a critical value of approximately 4/1

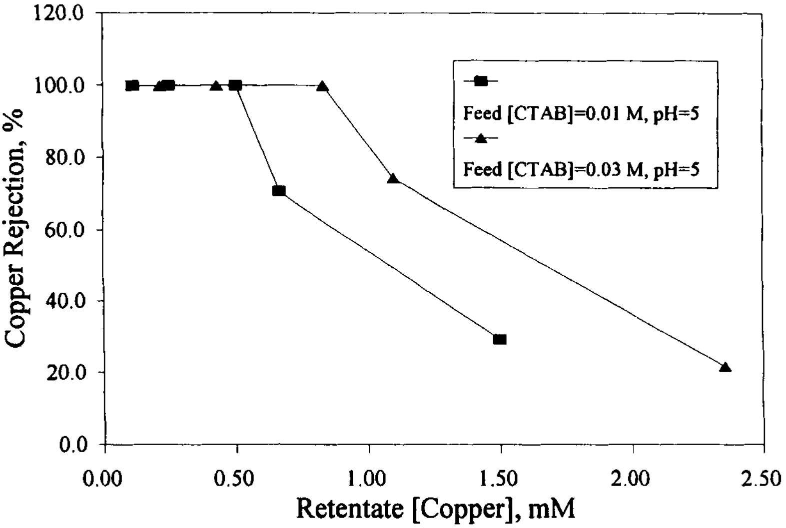

FIG. 7 Copper rejection as a function of retentate copper concentration with varying surfactant concentration.

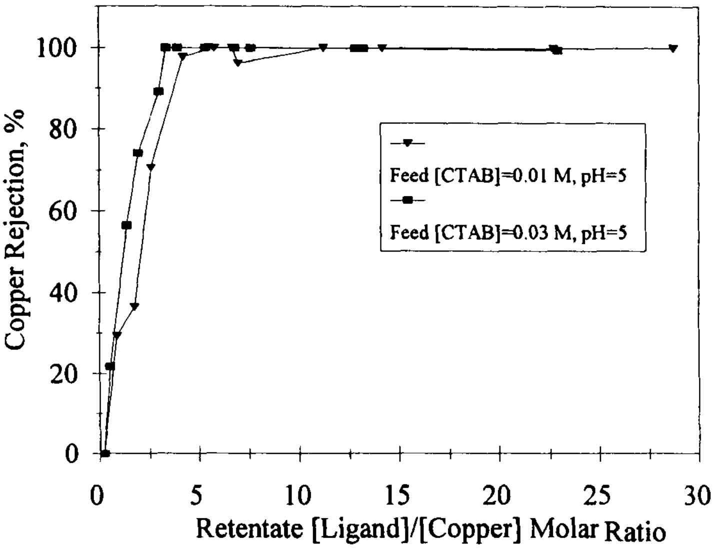

FIG. 8 Copper rejection as a function of initial ligand/copper molar ratio with varying surfactant concentration.

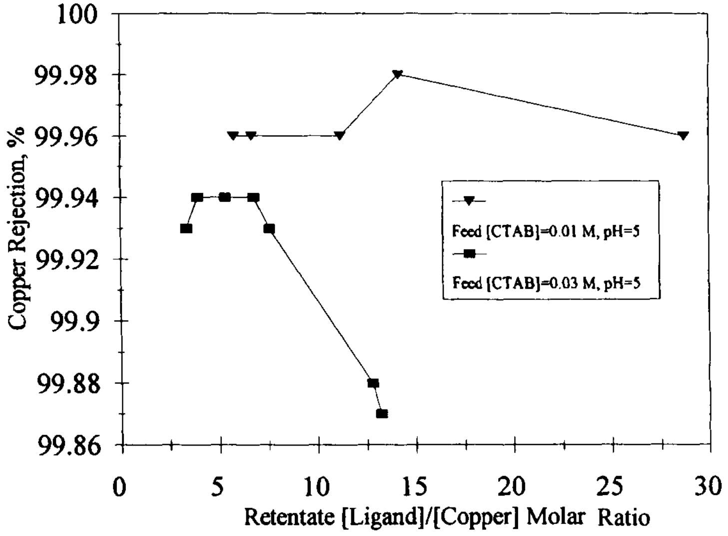

FIG. 9 Copper rejection as a function of initial ligand/copper molar ratio with varying surfactant concentration.

which is slightly dependent on the feed surfactant concentrations for high copper rejections. At a given feed CTAB concentration, the feed ligand and copper concentrations need to be below the ligand:copper complex solubility limit to avoid precipitation of the complex; this limit increases as the feed CTAB concentration increases since there is a higher concentration of micelles to solubilize the complex. We did not observe any precipitation under any experimental conditions used here or even at feed ligand and copper concentrations of 10 and 4 mM, respectively, in 30 mM CTAB. Table 2 and Figs. 7–9 summarize the effect of feed surfactant concentration and feed ligand/copper concentration ratio on copper rejection.

The effect of retentate calcium concentration on copper rejection and permeate/retentate concentration ratio of copper or calcium is shown in Table 3 and Figs. 10 and 11. The copper rejection slightly decreases with increasing retentate calcium concentration, probably due to competitive binding on the ligand. As seen in Fig. 11, the permeate [copper] to retentate [copper] molar ratio is on the order of 10^{-4} while the permeate [calcium] to retentate [calcium] molar ratio exceeds unity and is as high as 2 (calcium is "expelled" from the retentate due to the positively charged micelles). Therefore, selectivity is perfect for copper vs calcium while maintaining a very high separation factor.

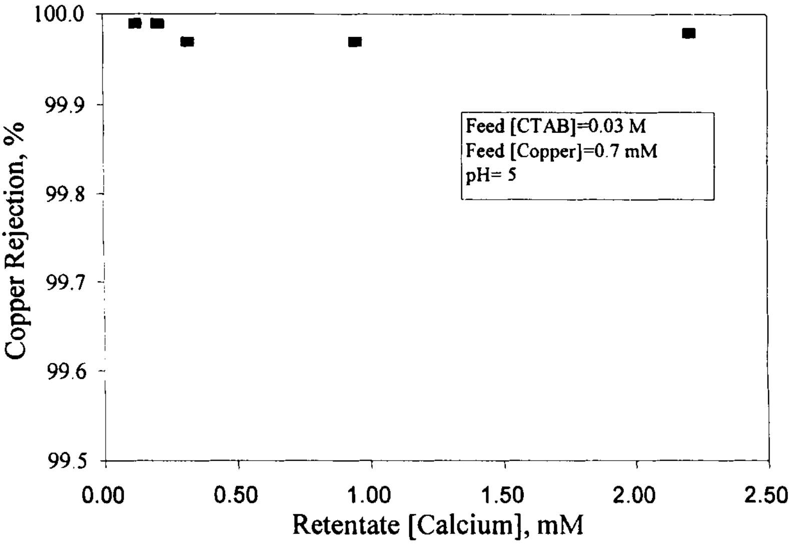

FIG. 10 Copper rejection as a function of retentate calcium concentration.

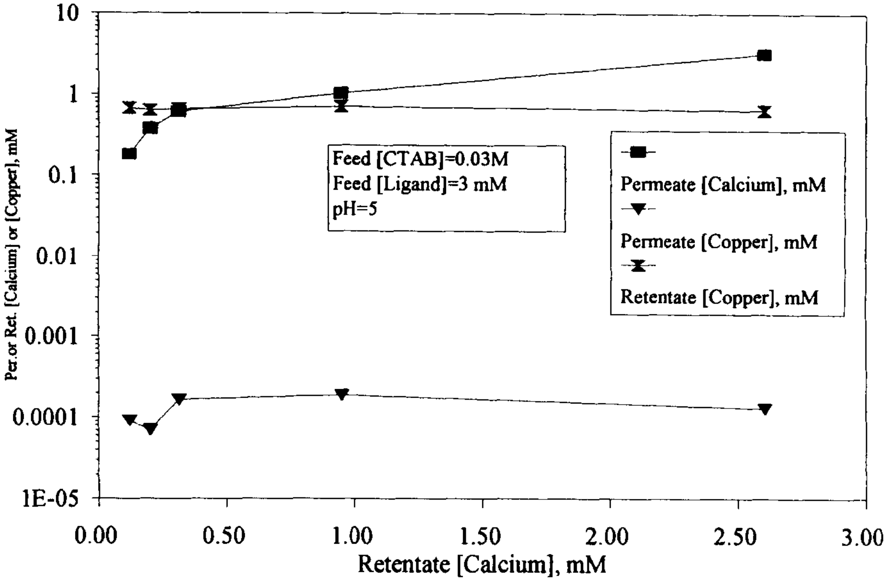

FIG. 11 Permeate or retentate calcium and copper concentration as a function of retentate calcium concentration.

The ligand and the CTAB separation efficiencies are shown in Figs. 12 and 13. Figure 12 shows ligand rejection as a function of retentate [ligand] for retentate solutions at pH values of 2 and 6. The plots show that ligand rejection decreases from approximately 99 to 97% as the retentate ligand concentration is increased, and slightly better rejections are observed at the high pH. The permeate [ligand] corresponds to the unsolubilized [ligand] in the retentate. The retentate [ligand] minus the unsolubilized retentate [ligand] is the solubilized retentate [ligand]. The retentate [CTAB] minus the permeate [CTAB] (discussed next) is the retentate micellized [CTAB]. The solubilization equilibrium constant (K) can be calculated from these values (33).

$$K = C_s/[(C_s + C_{mic})(C_{un})] \tag{6}$$

where C_s = solubilized retentate [ligand]
C_{mic} = retentate micellized [CTAB]
C_{un} = unsolubilized retentate [ligand]

The data in Fig. 12 can be used to calculate K for the ligand complexed with copper and in uncomplexed form at pH 2 and 6. The ligand in per-

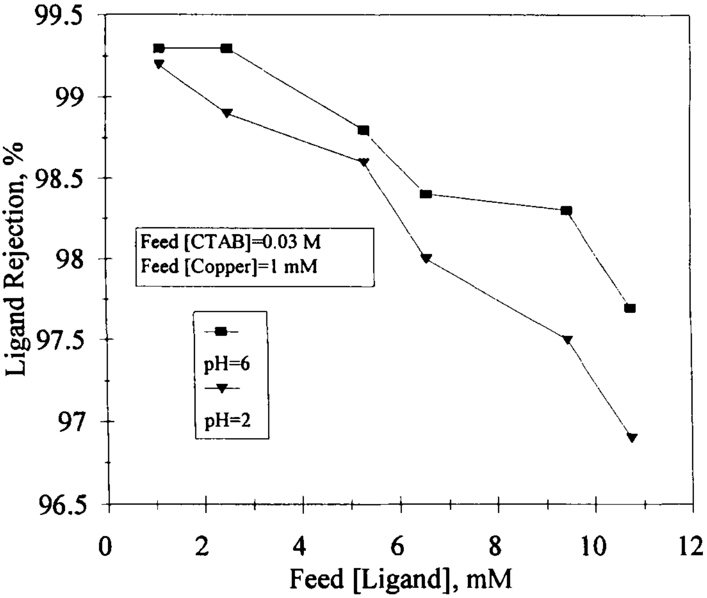

FIG. 12 Ligand rejection as a function of feed ligand concentration with varying pH.

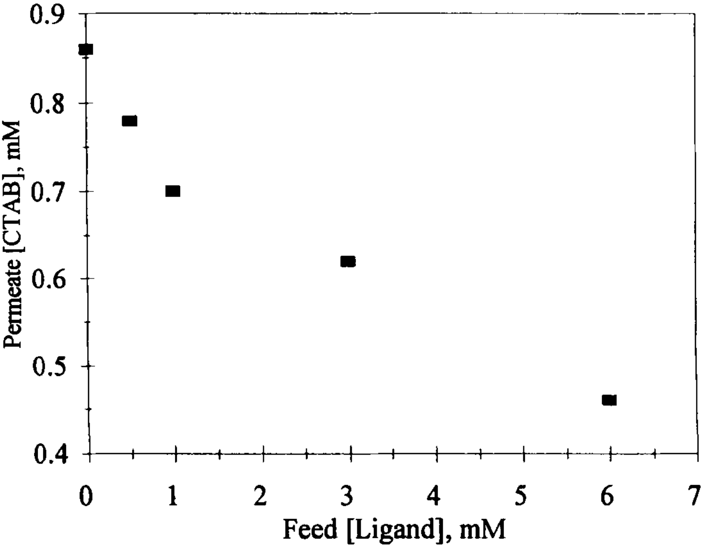

FIG. 13 Permeate CTAB concentration as a function of feed ligand concentration.

meate corresponds to both complexed and uncomplexed forms; however, it is reasonable to assume that at a ligand/copper molar ratio of far less than 2, almost all ligand is in complexed form. At a ligand/copper molar ratio of much greater than 2, the ligand in both retentate and permeate is mostly in uncomplexed form. Therefore, it is possible to determine K at these extreme conditions at both pH values. In complexed form $K = 4758$ M^{-1} at pH 6 and $K = 2500$ M^{-1} at pH 2. In uncomplexed form $K = 1071$ M^{-1} at pH 6 and $K = 848$ M^{-1} at pH 2. These K values indicate that the ligand is much more soluble in complexed form at both pH values and also more soluble at the higher pH.

The surfactant concentration in the permeate is approximately equal to the monomeric surfactant concentration in the retentate or the surfactant CMC (14, 15, 28). In addition, incorporation of an organic compound such as the ligand into micelles of the ionic surfactant tends to reduce the CMC (32–34) of the surfactant, causing a smaller concentration of monomers to pass through the membrane into the permeate. Figure 13 shows permeate [CTAB] as a function of feed [ligand]. For pure CTAB, the measured permeate concentration is 0.86 mM, which is in good agreement with a CMC value of 0.88 mM (23). As the ligand concentration is increased from 0.5 to 6 mM, the measured permeate [CTAB] declines to approximately 0.45 mM.

Regeneration of Retentate

In order for LM-MEUF to be economically attractive, the retentate solution needs to be regenerated (i.e., the surfactant and the ligand recovered for reuse). In traditional solvent extraction operations, copper is stripped from the loaded organic with sulfuric acid at a pH of about 2. The stripped solvent is then recycled back to the extraction circuit of the process (2, 3, 41). In this study the same principle is utilized to ion exchange H^+ for Cu^{2+} at low pH in the retentate from the LM-MEUF process, followed by a stripping ultrafiltration step. At this pH a large fraction of the copper complexed to the ligand can be replaced by H^+, allowing the now uncomplexed metal ions to pass through the membrane to the permeate while micelles with their solubilized ligand are retained in the retentate. The surfactant rejection should be very high (97–99%), similar to rejections measured during LM-MEUF since the CMC is anticipated to be very mildly affected by pH. However, ligand solubilization was shown to be affected by the pH of the solution.

All stripping (retentate regeneration) experiments were carried out under equilibrium conditions since there is ample evidence that these results very closely predict ultrafiltration results, as has already been discussed. The extent of retentate regeneration can be expressed in terms of stripping efficiency (in %).

$$\text{Stage Stripping Efficiency} = (100)(1 - (\text{Retentate Equilibrium } [Cu^{2+}]/\text{Feed } [Cu^{2+}])) \quad (7)$$

$$\text{Overall Stripping Efficiency} = (100)(1 - (\text{Final Stage Retentate } [Cu^{2+}]/\text{Feed } [Cu^{2+}])) \quad (8)$$

Stripping efficiencies for various retentate copper concentrations in 0.03 M feed CTAB and 3 mM feed ligand solutions are listed in Table 4 and Figs. 14 and 15. Figure 14 shows stage stripping efficiency as a function of stripping stage. Stage efficiency is the degree of copper separation achieved in one SED stage (one batch stage). If all Cu^{2+} were detached from the ligand by this acidification process (ion exchange), and the permeate copper anion/ion activity were the same in both permeate and retentate, then approximately 50% of the copper from the retentate should pass

TABLE 4
Copper Stripping Efficiency Using Sulfuric Acid: pH 2.0, Feed [ligand] = 3 mM, Feed [CTAB] = 0.03 M

Feed [copper] (mM)	Stripping stage	Copper stripping efficiency (%)	Retentate [copper] (mM)	Permeate [copper] (mM)
1.00	1	64.1	0.3	0.44
0.36	2	69.4	0.11	0.17
0.11	3	59.1	0.045	0.047
Overall copper stripping efficiency = 95.5				
3.00	1	64.3	1.07	1.4
1.07	2	66.3	0.36	0.5
0.36	3	58.3	0.15	0.2
Overall copper stripping efficiency = 95				
4.45	1	58.6	1.85	2.7
1.85	2	62.7	0.69	0.83
0.69	3	50.7	0.35	0.17
0.35	4	25.7	0.26	0.004
Overall copper stripping efficiency = 94.1				
9.00	1	70.1	2.7	3.84
3.84	2	67.4	1.25	1.86
1.25	3	62.4	0.47	0.83
0.47	4	61.7	0.18	0.27
Overall copper stripping efficiency = 98				

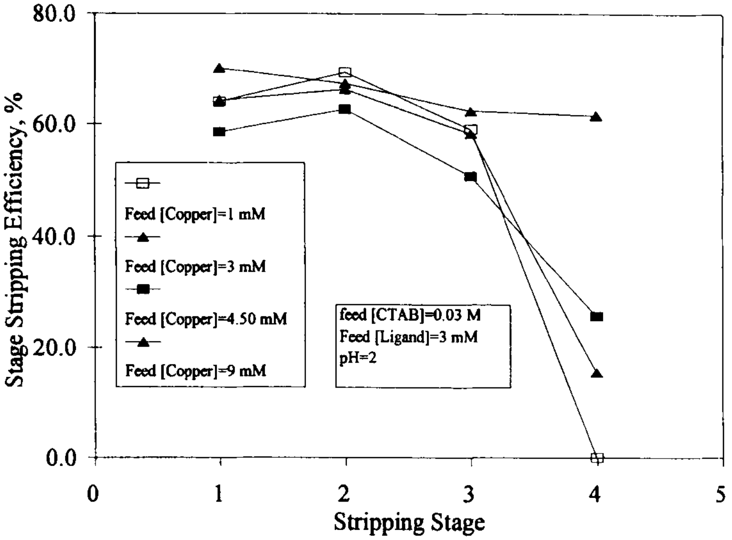

FIG. 14 Stage stripping efficiency as a function of stripping stage.

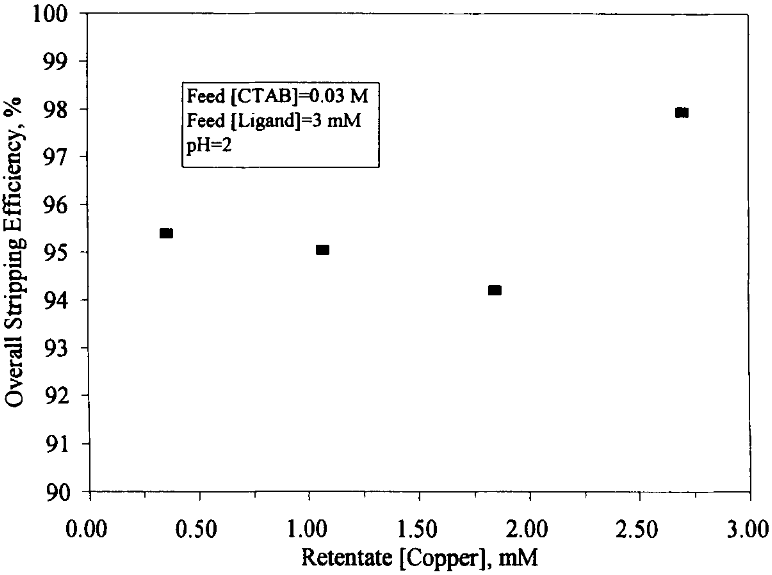

FIG. 15 Overall stripping efficiency as a function of retentate copper concentration.

through the membrane in each stage. Our results show that higher than expected equilibrium copper concentration is observed in the permeate due to some ion expulsion effect (4, 7, 8, 22, 27). To realize a better ultimate separation, the process can be staged. The retentate from one stage becomes the feed to the subsequent stage. Overall stripping efficiency is a cumulative value and represents copper separation obtained in several stages; it is a function of the number of stages used. Figure 15 shows that the overall stripping efficiency exhibits a minimum with retentate [copper]. Overall stripping efficiencies of greater than 94% are achieved in three to four stripping stages. These stripping efficiencies are dependent on the SED cell permeate/retentate ratio and do not directly relate to actual ultrafiltration stripping efficiencies although the ion distribution data can be used to design the number of ultrafiltration stages required to attain a desired degree of stripping in an actual process.

The permeate from the stripping ultrafiltration step contains Cu^{2+} and residual amounts of the surfactant and the ligand. The Cu^{2+} in this solution can be recovered by electrowinning (2, 3) or removed by lime precipitation. If the electrowinning option is chosen, the surfactant and the ligand can also be recovered and recycled. If the lime precipitation method is used, Cu^{2+} precipitates out as the hydroxide. The concentration of the surfactant in the stripping permeate is approximately equal to its CMC, as described before, while ligand losses have been determined experimentally as shown in Fig. 12. For both the ultrafiltration and stripping steps, integration of the point separation efficiencies obtained here over the retentate concentrations from inlet to outlet of an ultrafiltration device (e.g., spiral wound or hollow fiber) can yield the overall permeate composition from the unit. In designing a commercial LM-MEUF operation, flux must be considered in defining design parameters such as the feed surfactant concentration and the permeate/retentate product volume ratios. Flux studies have been reported for ultrafiltration of a number of surfactants (1, 15–17, 21, 28) which can be combined to design a complete LM-MEUF process with the results reported here.

ACKNOWLEDGMENTS

Financial support for this work was provide by National Science Foundation Grant CTS 9123388, an Applied Research Grant from the Oklahoma Center for the Advancement of Science and Technology. In addition, support was received from the industrial sponsors of the Institute for Applied Surfactant Research including Akzo Nobel, Amway Colgate-Palmolive, Dow, DowElanco, DuPont, Henkel, ICI, Kerr-McGee, Lever, Lubrizol, Nikko Chemical Phillips Petroleum, Pilot Chemical, Reckitt and Coleman, Shell, Sun, and Witco. Dr. Scamehorn holds the Asahi Glass Chair in chemical engineering at the University of Oklahoma. Henkel provided chemicals for this work.

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Received by editor December 9, 1996
Revision received February 1997