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USE OF MICELLAR-ENHANCED ULTRAFILTRATION AND
LIGAND-MODIFIED MICELLAR-ENHANCED ULTRAFILTRATION
PROCESSES TO REMOVE DISSOLVED METALS AND
ORGANIC SOLUTES FROM AQUEOUS STREAMS

A Dissertation

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the
degree of

Doctor of Philosophy

By

BITA FILLIPI
Norman, Oklahoma
1997
USE OF MICELLAR-ENHANCED ULTRAFILTRATION AND LIGAND-MODIFIED MICELLAR-ENHANCED ULTRAFILTRATION PROCESSES TO REMOVE DISSOLVED METALS AND ORGANIC SOLUTES FROM AQUEOUS STREAMS

A Dissertation APPROVED FOR THE
SCHOOL OF CHEMICAL ENGINEERING AND MATERIALS SCIENCE

BY

John Scamehorn
Chen-I D. Anstine
Rick W. Tyner
Jill Harrison
Lance Sobba
Dedicated to

My Best Friend and Husband, Greg and My Son, Michael

For Their Love and Encouragement
ACKNOWLEDGMENTS

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ABSTRACT

The effectiveness of micellar-enhanced ultrafiltration (MEUF) and ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) techniques for removal of heavy metal ions and/or organic pollutants from aqueous streams are studied. In MEUF metal ions bind to the surface of negatively charged micelles of an anionic surfactant while organic solutes dissolve inside the micelles. In LM-MEUF a surfactant and a ligand are added to a solution containing ions of like charge. The ligand complexes with the target ion of interest and incorporates inside the micelles. In both processes the mixture is passed through an ultrafiltration membrane with pore sizes small enough to reject the micelles and their associated ions or solubilized organics. In Chapter 1 the technical feasibility of LM-MEUF process for selective removal of copper from an aqueous solution using a commercial ligand in a cationic surfactant is investigated. The effect of pH, and the concentrations of copper, calcium, surfactant, and the ligand on the efficiency of copper removal are reported. A novel surfactant/ligand regeneration scheme is also introduced in this Chapter. Chapter 2 evaluates the economic feasibility of LM-MEUF based on the experimental results in Chapter 1. This Chapter includes a sensitivity analysis for several operating scenarios to determine the most favorable operating conditions. A comparative cost estimate is performed to assess the economic viability of LM-MEUF copper extraction process compared to the conventional copper extraction process. In Chapter 3 the advantages of addition of small concentrations of
nonionic surfactant to an anionic surfactant in MEUF system is discussed. The resulting anionic-nonionic mixture exhibits negative deviation from ideality of mixing which results in a larger fraction of the surfactant being present in micellar form. The contribution of concentration polarization and membrane charge to solute rejection is also studied; comparison of experimental solute rejections to those predicted by equilibrium models support the presence of these mechanisms.
CHAPTER 1

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

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-propanedione 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 is 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.
1.1 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 waste water 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 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 Figure I.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 waste water 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 co-workers 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 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 non-toxic 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.
1.2 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 (14,15-22,28,32). 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 to nearly 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 has 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:

\[
\text{Rejection} = (100)(1-\frac{[\text{solute in permeate}]}{[\text{solute in retentate}]}) \quad (1.1)
\]

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 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 volume concentrated retentate stream containing a large percentage of the surfactant/ligand/target ion, and a large
volume 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 are not significantly rejected by the ultrafiltration membrane. Therefore, the surfactant concentration in the permeate is approximately equal to the monomeric surfactant concentration in 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 opposite charge to that of surfactant tend 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\textsuperscript{2+} from a Cu\textsuperscript{2+}/Ca\textsuperscript{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\textsuperscript{2+} of greater than 99% were reported with no rejection of Ca\textsuperscript{2+} (4,5). Comparable rejections of Cu\textsuperscript{2+} have been observed using the ligand 4-hexadecyloxy- benzyliminodiacetic acid (BIDA) in CPC in the presence of Ca\textsuperscript{2+} with once again no rejection of Ca\textsuperscript{2+} (8). 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\textsuperscript{2+} in the LM-MEUF process. The ion expulsion of uncomplexed Ca\textsuperscript{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 I.2 is an integrated process flow diagram for the LM-MEUF process incorporating the stripping regeneration step.
1.3 EXPERIMENTAL

1.3.1 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-propanedione and its structure is shown in Figure I.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$_2$.2H$_2$O and CaCl$_2$.2H$_2$O were used as the source of copper and calcium ions. Copper chloride dihydrate and calcium chloride dihydrate are hygroscopic and they were dried in the 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.
1.3.2 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 micelles can occur in the permeate, but after 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 concentrations of $\text{Cu}^{2+}$ and $\text{Ca}^{2+}$ 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 (column packing: reverse phase C18) 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, the stripping experiments were staged; i.e., the permeate from the first SED cell (after semiequilibrium was 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 content of identical cells were analyzed; if there was less than 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.
1.4 RESULTS AND DISCUSSION

1.4.1 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 one percent, the value of the $K_{ML}$ must be at least $1 \times 10^7$ 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 metal-ligand complex in the solution is greater or equal to 99% of the total concentration of 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 confrontational freedom of the ligand in micelles become limited, causing alterations in metal:ligand complexation behavior.

Protonation and complexation equilibria pertinent to this investigation are given by Equations I.2-I.5.

Protonation of the ligand

\[ \text{HL} \leftrightarrow \text{L}^- + \text{H}^+ \]  \hspace{1cm} (I.2)

\[ K_a = \frac{[\text{L}^-][\text{H}^+]}{[	ext{HL}]} \]  \hspace{1cm} (I.3)

Metal-ligand complexation

\[ \beta_1 = \frac{[\text{ML}^+]}/[\text{M}^2+][\text{L}^-] \]  \hspace{1cm} (I.4)

\[ \beta_2 = \frac{[\text{ML}_2]}/[\text{M}^2+][\text{L}^-]^2 \]  \hspace{1cm} (I.5)

\( K_a \) represents the stepwise acid dissociation constant. Complex formation constants can be expressed as either stepwise constants, \( K_{\text{ML}_i} \), or cumulative formation constants, \( \beta_j \) (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 1.4 shows plots of the observed pH as a function of volume of NaOH added in these experiments. The titration data are fitted using computer programs PKAS (43) to determine a $K_a$ of $10^{-8.06}$. Figure 1.4 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 this data; $\beta_1 = 10^{6.79}$ and $\beta_2 = 10^{14.02}$. Equations 1.4 and 1.5 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 $\beta_1$ and $\beta_2$. The calculated values compare well to literature values for the same chelating group in water (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).
1.4.2 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 I.1-I.3 and Figures I.5-I.15. The data are plotted as rejections to illustrate the effectiveness of the separation, and as permeate copper concentration to illustrate data when rejections are high and trends in rejections are difficult to observe. Figure I.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 Cu²⁺ in the solution and incorporates 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 I.6 shows that at constant feed ligand concentration, increasing the pH causes a moderate increase in copper rejection. However, at a feed pH of 5, increasing the feed ligand concentration results in a significant increase in copper rejection. As shown in Figure I.6, at a retentate copper concentration of 1.5 mM, an
increase in feed ligand concentration from 1 to 6 mM results in an 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 Figures 1.7-1.9, it is critical to design a system where the feed ligand/copper molar ratio is above a critical value of approximately 4/1 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 mM and 4 mM respectively in 30 mM CTAB. Table I.2 and Figures I.7-I.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 I.3 and Figures I.10 and I.11. The copper rejection slightly decreases with increasing retentate calcium concentration probably due to competitive binding on the ligand. As seen in Figure I.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.

The ligand and the CTAB separation efficiencies are shown in Figures I.12 and I.13. Figure I.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).

\[ K = \frac{C_s}{(C_s + C_{mic})(C_{un})} \]  

(1.6)

where:

- \( C_s \) = solubilized retentate [ligand]
- \( C_{mic} \) = retentate micellized [CTAB]
- \( C_{un} \) = unsolubilized retentate [ligand]

The data in Figure 1.12 can be used to calculate K for the ligand complexed with copper and in uncomplexed form at pH of 2 and 6. The ligand in permeate corresponds to both complexed and uncomplexed forms, however it is reasonable to assume that at ligand/copper molar ratio of far less than 2, almost all ligand is in complexed form. At 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.
In addition, incorporation of organic compound such as the ligand into micelles of ionic surfactant tend to reduce the CMC (32-34) of the surfactant, causing smaller concentration of monomers to pass through the membrane into the permeate. Figure 1.13 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 mM to 6 mM the measured permeate [CTAB] declines to approximately 0.45 mM.
1.4.3 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 Cu²⁺ 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.

Stage Stripping Efficiency = \(100 \times (1 - \frac{\text{Retentate Equilibrium } [\text{Cu}^{2+}]}{\text{Feed } [\text{Cu}^{2+}]})\)  \(\text{(1.7)}\)

Overall Stripping Efficiency = \(100 \times (1 - \frac{\text{Final Stage Retentate } [\text{Cu}^{2+}]}{\text{Feed } [\text{Cu}^{2+}]})\)  \(\text{(1.8)}\)
Stripping efficiencies for various retentate copper concentrations in 0.03 M feed CTAB and 3 mM feed ligand solutions are listed in Table 1.4 and Figures 1.14 and 1.15. Figure 1.14 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 in each stage, approximately 50% of the copper from the retentate should pass through the membrane. 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 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 Figure 1.12. 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 with the results reported here to design a complete LM-MEUF process.
1.5 REFERENCES


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Table 1.2
Copper Rejection in 0.03 M CTAB (Feed)

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<td>Retentate, mM [Copper]</td>
<td>Retentate, mM [Calcium]</td>
<td>Permeate, mM [Copper]</td>
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Table 1.4

Copper Stripping Efficiency Using Sulfuric Acid

pH = 2.0, Feed [Ligand]=3 mM, Feed [CTAB]=0.03 M

<table>
<thead>
<tr>
<th>Feed [Copper], mM</th>
<th>Stripping Stage</th>
<th>Copper Stripping Efficiency</th>
<th>Retentate [Copper], mM</th>
<th>Permeate [Copper], mM</th>
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<tr>
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<td>0.045</td>
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</table>

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%
Figure I.1 Schematic of Traditional Copper Extraction Process

Copper Ore → LEACHING → EXTRATION → STRIPPING → Electrowinning

Sulfuric Acid

Loaded Organic

Stripped Organic

Copper and Sulfate Ions
Figure I.2 LM-MEUF Copper Extraction Process

Copper-Bearing Stream

Sulfuric Acid

CTAB Ligand

Extraction Unit pH = 5

Sodium Hydroxide

Retentate: CTAB/Ligand/Copper

Permeate: Water

Membrane

Recycled CTAB and Ligand

Membrane

Copper and Sulfate Ions

Lime

Electrowinning

Precipitated Copper Hydroxide

Retentate: CTAB/Ligand

Copper and Sulfate Ions

Permeate: Water

Membrane

Stripping Unit pH = 2
Figure I.3. Schematic of the ligand structure.
Figure I.4

Titration Results for CTAB/Ligand/Copper, 0.1 M NaOH

- [CTAB]/[Ligand]
- [CTAB]/[Ligand]/[Copper]

[CTAB]=0.03 M
[Ligand]=3 mM
[Copper]=1.5 mM
Solution Volume=25 mL
Figure I.5
Permeate [Copper] as a Function of Retentate [Copper]

Feed [CTAB]=0.01 M
pH=5

Feed [Ligand]=1 mM
Feed [Ligand]=3 mM
Feed [Ligand]=6 mM
Figure I.6

Copper Rejection as a Function of Retentate [Copper]

- Feed [CTAB]=0.01 M
- Feed [Ligand]=1 mM pH=3
- Feed [Ligand]=1 mM pH=5
- Feed [Ligand]=3 mM pH=3
- Feed [Ligand]=3 mM pH=5
- Feed [Ligand]=6 mM pH=3
- Feed [Ligand]=6 mM pH=5
Figure I.7

Copper Rejection as a Function of Retentate [Copper]

Feed [CTAB]=0.01 M, pH=5
Feed [CTAB]=0.03 M, pH=5
Figure I.8
Copper Rejection as a Function of Ligand/Copper Molar Ratio

Feed [CTAB]=0.01 M, pH=5
Feed [CTAB]=0.03 M, pH=5
Figure I.9
Copper Rejection as a Function of Ligand/Copper Molar Ratio

Feed [CTAB]=0.01 M, pH=5
Feed [CTAB]=0.03 M, pH=5
Figure I.10
Copper Rejection as a Function of Retentate [Calcium]

Feed [CTAB]=0.03 M
Feed [Copper]=0.7 mM
pH= 5
Figure I.11
Permeate or Retentate [Calcium] and [Copper] vs. Retentate [Calcium]

Feed [CTAB]=0.03M
Feed [Ligand]=3 mM
pH=5

Permeate [Calcium], mM
Permeate [Copper], mM
Retentate [Copper], mM

Feed [CTAB]=0.03M
Feed [Ligand]=3 mM
pH=5
Figure I.12
Ligand Rejection as a Function of Feed [Ligand]

Feed [CTAB]=0.03 M
Feed [Copper]=1 mM

- pH=6
- pH=2

Ligand Rejection, %

Retentate [Ligand], mM
Figure I.13

Permeate [CTAB] as a Function of Feed [Ligand]
Figure I.14
Stage Stripping Efficiency vs. Stripping Stage

- Feed [CTAB] = 0.03 M
- Feed [Ligand] = 3 mM
- pH = 2

- Feed [Copper] = 1 mM
- Feed [Copper] = 3 mM
- Feed [Copper] = 4.50 mM
- Feed [Copper] = 9 mM
Figure I.15
Overall Stripping Efficiency vs. Retentate [Copper]

Feed [CTAB]=0.03 M
Feed [Ligand]=3 mM
pH=2
CHAPTER 2
A Comparative Economic Analysis of Copper Removal From Water by Ligand-Modiﬁed Micellar-Enhanced Ultrafiltration and by Conventional Solvent Extraction

In ligand-modiﬁed micellar-enhanced ultraﬁltration (LM-MEUF), a surfactant and a ligand are added to an aqueous solution containing ions of like charge. The ligand forms a complex with the target ion of interest and becomes incorporated in the micelle. This solution is then treated by an ultraﬁltration process with membrane pore sizes small enough to reject the micelles and their solubilized metal ligand complexes. Previous studies have demonstrated the technical feasibility of LM-MEUF, with copper rejection exceeding 99% with no removal of calcium using several different ligands. The ability to regenerate the surfactant/ligand for reuse has also been shown. In this study, an economic analysis of LM-MEUF (with regeneration) for a $1 \times 10^5$ gallons/day unit is reported. The effects of important parameters were investigated; including feed surfactant, ligand, and copper concentrations. The results from the sensitivity analysis are used to compare the cost of LM-MEUF for copper removal and recovery to the conventional copper solvent extraction process. The comparative economic analysis indicates a 17% higher capital and a 43% higher operating cost for LM-MEUF process compared to the solvent extraction process.

Keywords: Surfactants, Copper Extraction, Economic Analysis, Ultraﬁltration, Ligands
2.1 INTRODUCTION

The discharge of organic and metal pollutants into the environment is a serious problem facing numerous industries. Wastewaters containing dissolved metal ions such as nickel, zinc and copper originate from a variety of sources such as photographic industries, refineries, abandoned metal mines, and metal plating operations. Effluents from the mining industry contain dissolved kerosene, ligands and heavy metals. The concentrations of dissolved organics and metals in wastewaters are highly regulated due to their toxicity even at extremely low concentrations. The stringent environmental and ecological requirements have spurred the search for industrial waste treatment options with low energy, labor, and capital costs.

Solvent extraction is widely utilized in metal recovery operations, including copper recovery, using oil soluble extractants (1). In metal recovery operations, the target metal ion such as copper is extracted from an aqueous solution (e.g., heap leach solution or effluent from a copper plating operation) into an organic solvent such as kerosene which contains the active reagent (2-5). 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, and high capital cost of the organic inventory of the plant (5). But even with solvents that are slightly water soluble, the high flow rate of wastewater results in substantial solvent loss which causes adverse environmental effects. Furthermore, solvent extraction is most suitable for removal of
solutesthat are present in high concentrations; for very dilute solutions the cost of power becomes high (6).

Several surfactant-based separation processes have been demonstrated to be effective in the removal of heavy metals and/or organic contaminants from wastewater streams. These processes can be less energy intensive, less expensive and environmentally safer than traditional separation techniques such as distillation and evaporation (7).

Micellar-enhanced ultrafiltration (MEUF) is a surfactant-based separation process that has been used to remove heavy metal ions and/or organic contaminants from dilute streams (8-15). The surfactant forms micelles which are spherical aggregates containing 50-150 surfactant molecules (23). In MEUF, ions with the same charge are removed with approximately equal rejection (12) since binding of the cations to the oppositely charged micelle surface is primarily electrostatic in nature. To enhance selectivity in MEUF, we have developed ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) (16-22). This method involves addition of an amphiphilic ligand and a surfactant to the contaminated solution under conditions where most of the surfactant is present as micelles. The ligand has a high degree of solubilization in the micelles and a tendency to selectively complex the target metal ion. In much of our past work on LM-MEUF (17-22) we synthesized the ligands used; however in our most recent study we used a commercially available ligand with a cationic surfactant for selective removal of copper (16).
In this paper, the cost of the LM-MEUF copper separation method is compared with the conventional copper solvent extraction process for a $1 \times 10^5$ gallons/day (gpd) plant with feed copper concentration of 190 ppm (3 mM) and with a discharge stream copper concentration of 4 ppm (0.063 mM). The following study also includes a sensitivity analysis for the LM-MEUF process to provide some optimization.

Where applicable, copper removal and recovery by the lime addition method is the least expensive option (24). However, the application of this technique is limited to concentrated streams and lacks selectivity for the target species, therefore, it is not appropriate to compare to either the LM-MEUF or solvent extraction processes.
2.2 BACKGROUND

The conventional solvent extraction processes became possible with the development of organic compounds called chelating agents or ligands (1) which bind to target metal ion and selectively extract the target metal from aqueous solutions into the organic solvent since the ligand is dissolved in the solvent (2). Once the copper has been extracted into the solvent via association with the ligand, the solvent is contacted with an acidic solution where the protons are present in much higher concentration than the metal. As a result, the H⁺ preferentially complexes with the ligand, "stripping" the metal from the ligand in a series of conventional mixer-settlers. The ligand/solvent is reused and the copper is now concentrated in the acidic/aqueous solution. The ligand complexation chemistry is defined by:

\[
[2R-H]_{org} + [M^{2+}]_{aq} \rightleftharpoons [R_2M]_{org} + [2H^+]_{aq} \rightleftharpoons [2R-H]_{org} + [M^{2+}]_{ac}
\]  

where R-H is the ligand in the organic phase (org), \(M^{2+}\) is the target metal ion in the aqueous phase (aq) or acidic solution (ac), \(R_2M\) is the ligand:metal complex in the organic phase, and \(H^+\) is the hydronium ion released from the ligand in aqueous stripping solution.

A simplified flow sheet of the solvent extraction process is shown in Figure II.1. Sometimes, the copper is recovered as solid metal by electrowinning; i.e., plating out onto cathodes in an electrowinning cell with inert lead alloy anodes and either copper sheets or rigid blanks of titanium as the cathode. At the cathode, copper ions are
reduced to copper metal, while oxygen evolves at the anode (2-5,25-27). The stripped or barren organic solvent returns to the extraction circuit. Lime induced precipitation (24) is another potential method of recovering copper in solid form (as hydroxide precipitate) from this solution instead of electrowinning. In solvent extraction of copper, the transfer of copper ions from the aqueous to the organic phase (extraction) and from organic to aqueous phase (stripping) is a reversible reaction and is controlled by adjusting the pH of the aqueous phase (25-27). Extraction efficiencies of greater than 95% of the copper in the feed are customary (1). The contamination of aqueous raffinate leaving the circuit with trace amounts of solvents like kerosene and ligand is of major concern from an environmental as well as economical point of view (2).

Surfactant-based separation techniques such as ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) have been used for selective removal of metal ions such as copper from aqueous streams (16-22). 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 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 has both the moiety needed to complex the target metal ion and a large hydrophobic group that will cause it to partition (solubilize) strongly into the micellar pseudophase hydrophobic interior. Once the ligand selectively complexes with the target ion of interest, the metal-ligand
complex will also become associated with the micelles through this solubilization phenomenon. This solution 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 complexed ions will also be rejected. The unsolublized ligand, uncomplexed ions, and surfactant monomers pass through the ultrafiltration membrane to the permeate side. Figure II. 2 shows a schematic of the LM-MEUF copper extraction process. A retentate rejection (in percent) is defined as:

\[
\text{Rejection} = (100) \left(1 - \frac{[\text{solute in permeate}]}{[\text{solute in retentate}]}\right)
\] (II.2)

The resulting permeate stream contains very low concentrations of the surfactant, target metal, and the ligand. 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) (28,29). 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. 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 permeate with low concentrations of contaminants. The permeate (purified) stream passing through the membrane can achieve a very high degree of purity by staging this process. Although the permeate contains only trace amounts of ligand and surfactant, the makeup cost for lost ligand and surfactant emitted with this stream can become substantial due to its large volume. One
possibility is to treat the permeate using foam fractionation where previous studies have
defined conditions at which 90% of the surfactant can be recovered and recycled back to
the process (30).

In foam fractionation, sparging air is introduced beneath the surface of the liquid to
form bubbles (30,31). Solute species such as the surfactant and its dissolved organics
adsorb on the surface of gas bubbles. As the bubbles rise to form foam, the adsorbed
materials travel with them to the liquid-gas interface. The foam is collected from the top
of the flotation cell. The collapsed foamate is much more concentrated in surfactant and
its dissolved organics, in this case ligand, than in the original process stream and this
material can be recycled and reused.

The retentate stream is much more concentrated and considerably smaller in volume
than the original process stream; therefore, further treatment or disposal of the process
stream is less expensive. For very dilute streams, the retentate can be 1000 times more
concentrated in the target metal than the permeate, indicating the power of the LM-
MEUF separation method. Other metal clean-up techniques, such as lime precipitation,
show a decrease in efficiency with a decrease in metal concentration while LM-MEUF
exhibits either an increase or no change in metal removal efficiency (13). The surfactant
monomers in the retentate are not rejected significantly by the ultrafiltration membrane.
Therefore, the concentration of monomeric surfactant in the retentate is approximately
equal to the total surfactant concentration in permeate or the surfactant CMC \((15,16,32)\).

In industrial usage of LM-MEUF, a substantial fraction of surfactant and ligand must be reused for economic feasibility. Therefore, after the "extraction ultrafiltration" unit, regeneration is achieved by placing a "stripping ultrafiltration" unit. The former closely approximates the stripping circuit of a mixer-settler unit in solvent extraction. In a stripping ultrafiltration step, sulfuric acid is added to the retentate from the extraction unit and the protons or hydronium ions displace the copper from the ligand. This solution is then ultrafiltered and the micelles and solubilized ligand are rejected and this retentate solution recycled to the extraction ultrafiltration unit \((16)\). The surfactant and the ligand rejections in the extraction ultrafiltration have shown to be very high \((97\%-99\%)\) and mildly affected by pH \((16)\). The permeate from the stripping ultrafiltration step is much smaller in volume than the permeate from the extraction unit but concentrated with \(\text{Cu}^{2+}\) and with trace amounts of the surfactant and the ligand. The permeate from this step is treated in a foam fractionation unit to recover the surfactant and the ligand. The permeate stream leaving the foam fractionation unit has high concentration of \(\text{Cu}^{2+}\) which can be recovered by electrowinning or precipitated out as the hydroxide by addition of lime.

Larger pore-size membranes are preferred in ultrafiltration to achieve larger fluxes, resulting in a lower membrane surface area requirements and lower capital and
membrane replacement costs. Formation of a gel layer adjacent to the membrane due to concentration polarization can limit the flux through the membrane (13,33). For concentration polarization to occur, the process stream must become highly concentrated with the surfactant. For example, the gel concentration (the concentration at which flux becomes zero) for one cationic surfactant is approximately 600 mM (33).

When concentrating the metal in the retentate at any point either in the extraction or the stripping ultrafiltration unit, the retentate surfactant concentration should be maintained at or below about 350 mM to avoid flux limitations (13,33). Previous studies have shown that MEUF can effectively block micelles and result in high rejection with membrane molecular weight cutoff (MWCO) of 20,000 or higher (13). The permeate surfactant concentration (approximately equal to monomer concentration or CMC in the retentate) can be reduced due to the presence of the ligand (16). Therefore the solubilized ligand actually reduces the surfactant losses in the permeate by increasing the fraction of surfactant in micelles.

Since the ligand-metal complex becomes incorporated in micelles; any increase in the ligand-metal complex concentration must be compensated by an increase in the micellar concentration to maintain a constant rejection. However, since the final retentate surfactant concentration is limited by its gel point, the application of the LM-MEUF process with both high rejections and high permeate/feed volumetric ratios becomes restricted to dilute streams; at high ligand concentrations in the retentate, at constant surfactant concentration, a lower percentage of the ligand may be solubilized.
as the micelle approaches saturation with the ligand, and substantial ligand leakage into permeate occurs.

In this study, the extraction of copper using a commercially available ligand, 1-phenyl-3-isoheptyl-1,3-propanedione (Lix54 from Henkel), with the cationic surfactant n-hexadecyltrimethylammonium bromide (CTAB) was used as the basis of the economic analysis performed. The most favorable scenario examined is then compared to the economics of conventional solvent extraction (using kerosene) for the same conditions. A feed stream rate of $1 \times 10^5$ gpd is used where the incoming feed copper concentration must be reduced from 190 ppm (3 mM) to 4 ppm (0.063 mM)
2.3 RESULTS AND DISCUSSION

2.3.1 Effect of Operating Conditions on LM-MEUF Economics

It is assumed that the process stream passes through a filtration unit for removal of suspended solids prior to entering the extraction ultrafiltration unit. Also, it is assumed that the stream enters the system at a pH of approximately 6; therefore no pH adjustment is required. In the LM-MEUF copper extraction process, the surfactant is concentrated both in the extraction and stripping ultrafiltration units. In this study, the surfactant has a gel point concentration of approximately 600 mM; therefore, the surfactant concentration is not permitted to exceed 350 mM at any point in this process. For all operating scenarios, the retentate surfactant concentration leaving the extraction ultrafiltration unit is set at 150 mM and the retentate surfactant concentration leaving the stripping unit is set at 350 mM. The permeate concentration of the surfactant and ligand vary, depending on the feed surfactant/ligand concentration ratio; these values have been determined experimentally for the system used here (16). For all cases studied, the permeates from the extraction and the stripping ultrafiltration stages are treated in a foam fractionation unit; hence, the calculated surfactant and ligand losses reflect the losses occurring in the purified water emitted from the foam fractionation unit.

Although CTAB was used in experimental studies, in this paper we utilize flux data for hexadecylpyridinium chloride (CPC) to estimate CTAB behavior; both are cationic surfactants with CMC of approximately 1 mM (23) and, both have displayed analogous
behavior in our previous ultrafiltration studies (11-22). More flux data are also available for CPC than CTAB.

2.3.1.1 Feed Surfactant Concentration in Extraction Ultrafiltration

The effect of feed (initial) surfactant concentration on permeate and retentate flow rates, surfactant and ligand losses, and permeate copper concentration after one extraction ultrafiltration stage was analyzed with constant feed copper and ligand concentrations of 1 mM and 5 mM, respectively. The feed surfactant concentration ranged from 5 to 80 mM.

Table II.1 and Figures II.3-II.5 present the results of this analysis. Figure II.3 shows that as feed surfactant concentration increases from 5 mM to 80 mM, permeate flow rate decreases while retentate flow rate increases. At a feed surfactant concentration of 80 mM, the retentate flow rate exceeds that of the permeate. Permeate flow rates in excess of 3 times that of the retentate are preferred in ultrafiltration units to reduce the cost associated with further processing of the retentate stream (13). Since the retentate surfactant concentration has been set at 150 mM, increasing feed surfactant concentration causes an increase in rejection of ligand and copper, but an increase in the flow rate of the retentate requiring further processing; therefore, optimum feed surfactant concentration is a balance of these two factors.
Figure II.4 shows that surfactant losses in the permeate remain reasonably constant with varying feed surfactant concentration. This is because the concentration of the surfactant in the permeate closely approximates the surfactant CMC (16,32,33). Experimental results indicated that addition of this ligand to the cationic surfactant CTAB resulted in up to 50% reduction in the CMC of the surfactant (16). At lower feed surfactant concentrations and at a constant ligand concentration, higher ligand/surfactant concentration ratios are present, resulting in a larger reduction in the CMC of the surfactant. Figure II.4 shows that ligand losses decline sharply with the increase in feed surfactant concentration. As the concentration of micelles increases, more ligand is solubilized in the micelles resulting in higher ligand rejections. A decrease in permeate flow rate also contributes to lower ligand losses. The permeate from the extraction ultrafiltration stage is treated in a foam fractionation unit where a recovery of 75% for the surfactant and the ligand is assumed. Previous experimental data (30) has shown that up to 90% of the cationic surfactant CPC can be recovered in eight foam fractionation stages with 45 minutes residence time. To be conservative, a recovery of 75% is assumed for the surfactant and the ligand in the foam fractionation process.

Figure II.5 shows the annual cost of surfactant and ligand losses as a function of feed surfactant concentration. The costs are based on $12/kg ligand, $2.1/kg surfactant, 365 operating days/yr, and 75% surfactant and ligand recovery in foam fractionation operations.
As shown in Table II.1, copper concentration in the permeate also declines with increasing surfactant concentration, partly because higher rejections are obtained at higher surfactant concentrations, but mostly due to the decrease in permeate flow rate.

2.3.1.2 Feed Ligand Concentration in Extraction Ultrafiltration

Table II.2 and Figures II.6-II.8 show the effect of feed ligand concentration on permeate and retentate flow rates, surfactant and ligand losses, and permeate copper concentration. All conditions are analogous to the preceding analysis with the exception that the feed copper and surfactant concentrations are now constant at 1 mM and 30 mM, respectively, while the feed ligand concentration is varied from 1 mM to 10 mM.

Figure II.6 shows that the permeate and retentate flow rates remain nearly constant with varying ligand concentration. This is expected since the feed and retentate surfactant concentrations are set at 30 mM and 150 mM respectively; therefore, the same degree of concentration is realized for each case. Figure II.7 shows surfactant and ligand losses in the permeate and the permeate copper concentration as a function of feed ligand concentration after one ultrafiltration stage. Surfactant losses decrease with an increase in feed ligand concentration while ligand losses increase. As already described, at constant total surfactant concentration, increasing the concentration of solubilized ligand results in a reduction in the monomeric surfactant concentration which consequently results in a decrease in surfactant loss in the permeate; surfactant loss is reduced by approximately 40% when feed ligand concentration increases from 1 mM to
However, the ligand losses increase sharply with the increase in the feed ligand concentration. This is because the micelles are approaching saturation with the ligand and the unsolubilized ligand passes through the membrane to the permeate side. From Figure II.7, permeate copper concentration drops sharply when the feed ligand concentration reaches 3 mM and remains fairly constant beyond a feed ligand concentration of 6 mM.

Figure II.8 shows the annual cost of surfactant and ligand losses as a function of feed ligand concentration and the effect of permeate flow on these costs. The surfactant cost is nearly invariant with ligand feed concentration. The ligand cost increases about 5 fold with the increase in feed ligand concentration from 3 mM to 10 mM.

2.3.1.3 Feed Copper Concentration in Extraction Ultrafiltration

Table II.3 and Figures II.9-II.11 show the effect of feed copper concentration on permeate and retentate flow rates and surfactant and ligand losses after one ultrafiltration stage. The feed surfactant and ligand concentrations are held constant at 30 mM and 10 mM, respectively. Figure II.9 shows that permeate and retentate flow rates remain constant with varying feed copper concentration. This is because the feed and retentate surfactant concentrations are set at 30 mM and 150 mM for each case. Figure II.10 shows that the surfactant and ligand losses also remain constant at various copper concentrations. Figure II.10 shows that as feed copper concentration exceeds approximately 3 mM, the permeate copper concentration exceeds the desired 4 ppm.
concentration at the given surfactant and ligand concentrations. This is because copper rejection decreases drastically once the ligand/copper molar concentration ratio falls below 3:1 (16). Figure II.11 shows that the cost of surfactant and ligand losses are not affected by the increase in feed copper concentration since these values were held constant for this case.

2.3.1.4 Number of Stages in Extraction Ultrafiltration

In all cases discussed thus far, it has been assumed that the feed stream is treated in only one ultrafiltration stage regardless of its copper content. The effect of varying only one operating condition on the economics of the process while keeping other factors constant was analyzed. The permeate copper concentration was permitted to vary (Figures II.4 and II.7). The results from these single stage calculations are utilized to select the feasible feed surfactant and ligand concentrations for a given copper concentration, while maximizing the permeate flow rate in multistage calculations. For comparative economics, reduction of copper concentration by the same fraction must be compared. Therefore, if sufficient reduction in copper concentration is not attained in one stage, the number of stages required was calculated; this obviously can have a large effect on capital cost among other factors.

The results of this analysis are presented in Table II.4 and Figures II.12-II.14. Figure II.12 shows the increase in retentate flow rate and subsequently the decrease in permeate flow rate with the increase in feed copper concentration as discussed previously.
II.13 shows the surfactant and ligand losses and the required number of ultrafiltration stages as a function of feed copper concentration. Overall, the surfactant and ligand losses exhibit a decrease with the increase in copper concentration due to the decrease in permeate flow. Once the feed copper concentration reaches 254 ppm (4 mM), a second ultrafiltration stage must be incorporated to sustain the permeate copper concentration of 4 ppm. The permeate from the first ultrafiltration stage enters a second ultrafiltration unit to further reduce its copper content. More surfactant and ligand are added to the feed to this stage and once again the retentate surfactant concentration is fixed at 150 mM. The retentates from the first and second ultrafiltration stages combine and enter the stripping ultrafiltration stage. The permeate from the second ultrafiltration stage is treated in a foam fractionation unit to recover the surfactant and the ligand. Figure II.14 shows the annual cost of surfactant and ligand losses as a function of feed copper concentration. Although ligand mass losses are less than surfactant losses in this scenario, the annual cost of lost ligand is much higher than the surfactant due to higher ligand cost/kg.

2.3.1.5 Stripping Ultrafiltration

The feed to the stripping ultrafiltration step is the combined retentates from all of the extraction ultrafiltration stages. This feed is highly concentrated in copper, ligand, and surfactant. The copper can be stripped from the ligand by addition of sulfuric acid (e.g., 50 g/L) (2,16). The surfactant concentration in the feed to the stripping section is 150 mM and the retentate leaving the stripping stage has a surfactant concentration of 350
mM. This retentate stream has been largely depleted of copper (by addition of sulfuric acid), yet contains high concentrations of the ligand and the surfactant and is recycled as feed in the extraction ultrafiltration process. The permeate stream from the stripping unit is concentrated in copper and has trace amounts of the ligand and the surfactant; this permeate is treated in a foam fractionation unit for surfactant and ligand recovery. The copper (presented as Cu$^{2+}$) in the stream leaving the fractionation unit is precipitated with addition of lime.

Table II.5 and Figures II.15-II.17 show the results of this analysis of the stripping step. Figure II.15 shows the stripping permeate and retentate flow rates as a function of stripping feed copper content. Stripping permeate flow rate is slightly higher than stripping retentate flow rate in each case. The stripping feed flow rate increases with an increase in stripping feed copper concentration, therefore, both permeate and retentate flow rates increase. Figure II.16 shows the stripping permeate content of copper, ligand, and surfactant as a function of stripping feed copper content. The stripping permeate ligand content is slightly higher than its surfactant content; however, the ligand cost is substantially higher than the surfactant cost as shown in Figure II.17.
2.3.2 CAPITAL AND OPERATING COST COMPARISONS

The capital and operating cost estimates for both LM-MEUF and solvent extraction processes are based on $1 \times 10^5$ gpd unit with a feed copper content of 3 mM (190 ppm). The permeate stream from the LM-MEUF process and the raffinate stream from the solvent extraction process are required to have copper contents of no greater than 0.063 mM (4 ppm). The feed to both operations is regarded as waste or an effluent stream with little value; therefore, no feed costs are included in these estimates. Feed pretreatment options such as filtration are assumed to be the same for both processes and hence no cost data on pretreatment are presented here. Furthermore, it is assumed that the feed stream is at the desired pH and that no pH adjustments are necessary. Separation agent (solvent or surfactant/ligand) recovery processes are assumed to be similar for both operations; i.e., an adsorbing colloid flotation unit is assumed for solvent recovery in solvent extraction while a foam fractionation unit is used in LM-MEUF. The capital cost for each unit depends on the process stream flow rate. Since the raffinate stream from solvent extraction and the permeate stream from LM-MEUF have similar flow rates, these capital costs are assumed to cancel out and therefore are not included since this is a comparative economic analysis. Separation agent losses are calculated assuming the presence of these recovery units. In both processes, it is assumed that the copper is stripped with 50 g/l H$_2$SO$_4$. The stripping permeate from the LM-MEUF process or the aqueous stream from the stripping section of solvent extraction process have much smaller volume than the original process stream and are
much more concentrated in copper. The lime addition method is used to precipitate Cu\(^{2+}\) in both cases.

2.3.2.1 Capital Cost Estimation

The capital costs for both processes is estimated based on applying a series of factors to purchased equipment or installed equipment cost. The cost calculations in this study are conducted using the Chilton factors method (35). Indirect cost elements presented in operating expenses depend on capital cost since they are computed as a percentage of both capital and direct operating expenses.

The capital cost for the solvent extraction plant depends on the feed flow rate (36). In a typical plant, the extraction and stripping stages are operated with a fixed organic/aqueous ratio for operational stability and high stage efficiencies. An organic/aqueous volume ratio of one is used for mixer emulsions. The solvent extraction unit includes three extraction and one stripping stages with a mixer residence time of 3 minutes. Uninstalled equipment costs were obtained from Hazen-Quinn Inc.

The capital cost for the LM-MUEF plant depends on feed flow rate as well as the feed metal ion concentration. The cost for skid mounted units was obtained from published cost estimates (13,37) and vendor quotes. The skid mounted units require minor modification; therefore, the installation, piping, and instrumentation costs are all incorporated in the skid mounted unit cost. Tables II.6 and II.7 present capital cost.
estimates for solvent extraction and LM-MEUF copper extraction processes respectively. The capital cost of the LM-MEUF process is higher than that of solvent extraction by approximately 17%.

2.3.2.2 Operating Cost Estimation

The total annual expenses are the basis for calculating operating costs. The operating costs are either actual or those obtained by applying multiplication factors to the major components such as operating labor and plant investment (35,38).

The sources of data for the operating cost estimate for the solvent extraction process are: technical consultants, plant operating data, handbooks, and technical articles, among others. The data were then manipulated to arrive at the cost for a unit of the stated size. For large scale solvent extraction plants, the charges for the makeup quantities of entrained solvent (kerosene and ligand) in the raffinate are substantial. On average, this entrainment rate is 0.1 gallons solvent/1000 gallons raffinate (Lix54 is assumed to have a concentration of 1.5% vol/vol kerosene). Installation of solvent recovery equipment reduces the entrainment rate by half (1). Additional solvent losses occur due to evaporation, winds, and solar radiation which are included in total solvent loss shown in operating cost estimates. Since the quantity of metal that needs to be removed is small, the amount of solvent needed is small, and the reagent cost becomes unimportant compared to operating labor cost in this study.
Operating cost data for the LM-MEUF process are based on the results of the sensitivity studies, previous published cost data (13,37), and application of multiplication factors to the major costs (35,38).

Tables II. 8 and II.9 summarize operating cost estimates for the solvent extraction and the LM-MEUF processes, respectively. The LM-MEUF operating costs are higher than the solvent extraction cost by a factor of 1.43, mainly due to its higher reagent and power costs.
2.4 CONCLUSIONS

The main objective of this study is to provide approximate comparative economics of the LM-MEUF and the solvent extraction process. At this point in the development of LM-MEUF for various applications, it is important to determine if LM-MEUF process were much more economical than solvent extraction; in that case, great incentive for further development of LM-MEUF would be apparent. If the opposite were true, there would be little short term economic incentive for further incremental improvement in the technology. The results of the assessment can also guide future research in LM-MEUF by identifying areas of substantial potential cost reduction. A comparison of the costs indicate that the LM-MEUF process does not have a considerable advantage compared to a conventional solvent extraction process, particularly with respect to economy of the solvent needed. The LM-MEUF process showed a 17% higher capital and a 43% higher operating cost for a \(1 \times 10^3\) gallons/day unit. The higher operating cost for LM-MEUF is mainly due to its higher reagent and electrical costs. The operating cost for LM-MEUF can be reduced by using a surfactant with a higher gel point concentration and a lower CMC. A higher gel point concentration means that the surfactant in the feed stream can become more concentrated which consequently will reduce the retentate volume causing a reduction in the amount of sulfuric acid needed for successful stripping of copper ions. Using a surfactant with a lower CMC results in a smaller concentration of monomeric surfactant passing across the membrane to the permeate side. Furthermore, a surfactant with a lower CMC would cause higher micellar
concentration, resulting in more ligand being solubilized in the surfactant, reducing ligand losses. Therefore, it is possible for the LM-MEUF process to become more competitive if a different surfactant would be found with appropriate properties.
2.5 REFERENCES


(25) G. Eggett, D. Naden, Development in anodes for pure copper electrowinning from solvent extraction produced electrolytes, Hydrometallurgy 1 (1975) 123.


Table II. 1
Effect of Varying Surfactant Concentration
At Constant Feed Copper and Ligand Concentrations
on Relevant Variables Using One Extraction Ultrafiltration
Stage, Feed [Copper]=1 mM, Feed [Ligand]=5 mM

<table>
<thead>
<tr>
<th>Feed [Surfactant] mM</th>
<th>Permeate Surfactant Content Kg/d</th>
<th>Permeate Ligand Content Kg/d</th>
<th>Flow rate Permeate gpd</th>
<th>Retentate gpd</th>
<th>Cost of Makeup Surfate $/yr</th>
<th>Cost of Makeup Ligand $/yr</th>
<th>Permeate [Copper] ppm</th>
</tr>
</thead>
<tbody>
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Table II. 2
Effect of Varying Ligand Concentration
At Constant Feed Copper and Surfactant Concentrations on
Relevant Variables Using One Extraction Ultrafiltration Stage
Feed [Copper]=1 mM, Feed [Surfactant]=30 mM

<table>
<thead>
<tr>
<th>Initial [Ligand] mM</th>
<th>Permeate Surfactant Content Kg/d</th>
<th>Permeate Ligand Content Kg/d</th>
<th>Flow rate Permeate Retentate gpd</th>
<th>Cost of Makeup Surfactant $/yr</th>
<th>Cost of Makeup Ligand $/yr</th>
<th>Permeate [Copper] ppm</th>
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<td>80160</td>
<td>6379</td>
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Table II. 3
Effect of Varying Copper Concentration
At Constant Feed Ligand and Surfactant Concentrations on Relevant Variables in One Extraction Ultrafiltration Stage
Feed [Ligand]=10 mM, Feed [Surfactant]=30 mM

<table>
<thead>
<tr>
<th>Initial [Copper] mM</th>
<th>Permeate Surfactant Content Kg/d</th>
<th>Permeate Ligand Content Kg/d</th>
<th>Flow rate Permeate gpd</th>
<th>Cost of Makeup Surfactant $/yr</th>
<th>Cost of Makeup Ligand $/yr</th>
<th>Permeate [Copper] ppm</th>
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<td>80160</td>
<td>6379</td>
<td>110898</td>
<td>0.02</td>
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<td>8.3</td>
<td>25.2</td>
<td>80160</td>
<td>6379</td>
<td>110898</td>
<td>0.03</td>
</tr>
<tr>
<td>1</td>
<td>8.3</td>
<td>25.2</td>
<td>80160</td>
<td>6379</td>
<td>110898</td>
<td>0.06</td>
</tr>
<tr>
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<td>110898</td>
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<td>175.0</td>
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<td>110898</td>
<td>233.8</td>
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TABLE II.4
Effect of Varying Feed Copper, Surfactant, and Ligand Concentrations on the Number of Ultrafiltration Stages
Permeate [Copper] = 4 ppm

<table>
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<tr>
<th>Feed [Copper] mM</th>
<th>Feed Surfactant mM</th>
<th>Feed Ligand mM</th>
<th>Permeate Surfactant Content Kg/d</th>
<th>Permeate Ligand Content Kg/d</th>
<th>Flow rate Permeate gpd</th>
<th>Flow rate Retentate gpd</th>
<th>Cost of Makeup Surfactant $/yr</th>
<th>Cost of Makeup Ligand $/yr</th>
<th>Number of UF Stages</th>
</tr>
</thead>
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<td>11098</td>
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* Corresponds to the Feed Surfactant and Ligand Concentrations for Each Ultrafiltration Stages
### Table II. 5
Variables Related to Stripping Ultrafiltration Stage

Stripping Retentate [Surfactant]=350 mM

<table>
<thead>
<tr>
<th>Feed to Stripping Unit [Copper] Kg/d</th>
<th>Stripped Permeate Flow Rate Kg/d</th>
<th>Stripped Permeate Retentate Kg/d</th>
<th>Stripped Permeate Content Copper Kg/d</th>
<th>Stripped Permeate Content Ligand Kg/d</th>
<th>Cost of Makeup Surfactant $/yr</th>
<th>Cost of Makeup Ligand $/yr</th>
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<tr>
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<td>0.35</td>
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Table II. 6  
Capital Cost For  
Solvent Extraction Plant 

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<td>Building and Site Development</td>
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<table>
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<th>Indirect Costs:</th>
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<td>Engineering and Construction</td>
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<td>Contractor Fee</td>
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<tr>
<td>Startup</td>
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<td>Other (legal and Finance)</td>
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</table>

| Total Depreciable Investment           | $712,000 |
| Land                                   | $14,000 |
| Working Capital                        | $21,000 |
| **Total Capital Investment**           | **$742,000** |
Table II. 7  
**Capital Cost For**  
**LM-MEUF Plant**

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<th>Description</th>
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<tr>
<td><strong>Indirect Costs:</strong></td>
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<tr>
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<td>Contractor Fee</td>
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<tr>
<td>Other (legal and Finance)</td>
<td>$5,000</td>
</tr>
<tr>
<td><strong>Total Depreciable Investment</strong></td>
<td>$828,000</td>
</tr>
<tr>
<td>Land</td>
<td>$17,000</td>
</tr>
<tr>
<td>Working Capital</td>
<td>$25,000</td>
</tr>
<tr>
<td><strong>Total Capital Investment</strong></td>
<td>$870,000</td>
</tr>
</tbody>
</table>
### Table II. 8
Annual Operating Cost For Solvent Extraction Plant

<table>
<thead>
<tr>
<th>Reagent Cost:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Kerosene ($1/gal)</td>
<td>$4,000</td>
</tr>
<tr>
<td>Ligand ($12/kg)</td>
<td>$5,000</td>
</tr>
<tr>
<td>Sulfuric Acid ($15/ton)</td>
<td>$2,000</td>
</tr>
<tr>
<td>Lime ($30/ton)</td>
<td>$800</td>
</tr>
<tr>
<td>Power ($0.08/kwh)</td>
<td>$4,500</td>
</tr>
<tr>
<td>Operating Labor ($15/hr)</td>
<td>$131,000</td>
</tr>
<tr>
<td>1 operator/shift</td>
<td></td>
</tr>
<tr>
<td>Maintenance Labor and Equipment</td>
<td>$21,000</td>
</tr>
<tr>
<td>Direct Supervision</td>
<td>$13,000</td>
</tr>
<tr>
<td>Labor Burden</td>
<td>$40,000</td>
</tr>
<tr>
<td>Overhead</td>
<td>$35,000</td>
</tr>
<tr>
<td>Insurance and Taxes</td>
<td>$11,000</td>
</tr>
<tr>
<td>Control Lab</td>
<td>$25,000</td>
</tr>
<tr>
<td>Depreciation (over 20 years)</td>
<td>$37,000</td>
</tr>
<tr>
<td><strong>Total Operating Cost</strong></td>
<td><strong>$329,300</strong></td>
</tr>
</tbody>
</table>
Table II. 9
Annual Operating Cost For
LM-MEUF Plant

<table>
<thead>
<tr>
<th>Reagent Cost:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant ($2.1/kg)</td>
<td>$14,500</td>
</tr>
<tr>
<td>Ligand ($12/kg)</td>
<td>$84,500</td>
</tr>
<tr>
<td>Sulfuric Acid ($15/ton)</td>
<td>$20,000</td>
</tr>
<tr>
<td>Lime ($30/ton)</td>
<td>$1,200</td>
</tr>
<tr>
<td>Membrane Cleaning</td>
<td>$4,000</td>
</tr>
<tr>
<td>Power ($0.08/kwh)</td>
<td>$26,000</td>
</tr>
<tr>
<td>Operating Labor ($15/hr)</td>
<td>$131,000</td>
</tr>
<tr>
<td>1 operator/shift</td>
<td></td>
</tr>
<tr>
<td>Maintenance Labor and Equipment</td>
<td>$24,000</td>
</tr>
<tr>
<td>Direct Supervision</td>
<td>$13,000</td>
</tr>
<tr>
<td>Labor Burden</td>
<td>$40,000</td>
</tr>
<tr>
<td>Overhead</td>
<td>$35,000</td>
</tr>
<tr>
<td>Insurance and Taxes</td>
<td>$13,000</td>
</tr>
<tr>
<td>Control Lab</td>
<td>$25,000</td>
</tr>
<tr>
<td>Depreciation (over 20 years)</td>
<td>$41,000</td>
</tr>
<tr>
<td><strong>Total Operating Cost</strong></td>
<td><strong>$472,200</strong></td>
</tr>
</tbody>
</table>
Figure II.1 Schematic of Solvent Extraction Process
Figure II.2 Schematic of LM-MEUF Process
Figure II.3
Permeate or Retentate Flow Rate vs. Feed [Surfactant], Constant Feed [Ligand] and [Copper], Single Stage Ultrafiltration Unit
Figure II. 4
Surfactant and Ligand Losses in Permeate vs. Feed [Surfactant], Constant Feed [Ligand] and [Copper], Single Stage Ultrafiltration Unit

Feed [Copper] = 1 mM
Feed [Ligand] = 5 mM

Permeate Surfactant
Permeate Ligand
Permeate [Copper]
Figure II.5
Annual Cost of Surfactant or Ligand vs. Feed [Surfactant], Constant Feed [Ligand] and [Copper], Single Stage Ultrafiltration Unit
Figure II.6
Permeate or Retentate Flow Rate vs. Feed [Ligand], Constant Feed [Surfactant] and [Copper], Single Stage

Feed \[\text{Copper}\]=1\ mM
Feed \[\text{Surfactant}\]=30\ mM
One Ultrafiltration Stage

Flow Rate, gpd

<table>
<thead>
<tr>
<th>Feed [Ligand], mM</th>
<th>Permeate</th>
<th>Retentate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Figure II.7
Surfactant and Ligand Losses in Permeate vs. Feed [Ligand], Constant Feed [Surfactant] and [Ligand], Single Stage Ultrafiltration Unit

Feed [Copper]=1 mM
Feed [Surfactant]=30 mM
Figure II.8
Annual Cost of Surfactant or Ligand vs. Feed [Surfactant], Constant Feed [Ligand] and [Copper], Single Stage Ultrafiltration Unit
Figure II. 9
Permeate or Retentate Flow Rate vs. Feed [Copper], Constant Feed [Surfactant] and [Ligand], Single Stage Ultrafiltration Unit
Figure II.10
Surfactant and Ligand Losses in Permeate vs. Feed [Copper], Constant Feed [Surfactnat] and [Ligand], Single Stage Ultrafiltration Unit

Feed [Surfactant] = 30 mM

Permeate Surfactant
Permeate Ligand
Permeate [Copper]

Feed [Copper], mM
Figure II. 11
Annual Cost of Surfactant and Ligand vs. Feed [Copper], Single Stage Extraction Ultrafiltration
Constant Feed [Surfactant] and [Ligand]
Figure II.12
Permeate or Retentate Flow Rate vs. Feed [Copper] with Variable Feed [Surfactant] and [Ligand] to Maintain a Permeate [Copper] = 4 ppm, Multistage Ultrafiltration Unit

Variables: Feed [Surfactant] and [Ligand]
Permeate [Copper] = 4 ppm

Flow Rate, gpd

0 1 2 3 4 5 6

Feed [Copper], mM
Figure II. 13
Surfactant and Ligand Losses in Permeate vs. Feed [Copper] to Maintain a Permeate [Copper] = 4 ppm, Multistage Ultrafiltration Unit
Figure II.14
Annual Cost of Surfactant and Ligand vs. Feed [Copper] with Variable Feed [Surfactant] and [Ligand] to maintain a Permeate [Copper]=4 ppm, Multistage Ultrafiltration Unit.
Figure II.15
Stripping Permeate or Retentate Flow Rate vs. Stripping Feed Copper Content, Single Stage Ultrafiltration Unit
Figure II.16
Surfactant and Ligand Losses in Stripping Permeate vs. Stripping Feed Copper Content, Single Stage Stripping Ultrafiltration Unit

![Graph showing surfactant and ligand losses in stripping permeate vs. stripping feed copper content.]

- **Copper**
- **Ligand**
- **Surfactant**

Stripping Feed Copper Content, Kg/d

Losses in Permeate, Kg/d
Figure II.17
Annual Cost of Surfactant and Ligand vs. Stripping Feed Copper Content, Single Stage Stripping Ultrafiltration Unit
CHAPTER 3

Use of Micellar-Enhanced Ultrafiltration at Low Surfactant Concentrations and with Anionic/Nonionic Surfactant Mixtures

Micellar-enhanced ultrafiltration (MEUF) is a separation technique which can be used to remove metal ions or dissolved organics from water. Metal ions bind to the surface of negatively charged micelles of an anionic surfactant while organic solutes tend to dissolve or solubilize within the micelles. The mixture is then forced through an ultrafiltration membrane with pore sizes small enough to block passage of the micelles and associated metal ions and/or dissolved organics. Monomeric or unassociated surfactant passes through the membrane and does not contribute to the separation. This paper considers advantages of addition of small concentrations of nonionic surfactant to an anionic surfactant; the resulting anionic/nonionic mixed micelles exhibit negative deviation from ideality of mixing which leads to a smaller fraction of the surfactant being present as monomer, and a subsequently larger fraction present in the micellar form. The addition of nonionic surfactant improved the separation of divalent zinc substantially at total concentrations above the CMC of the anionic surfactant. Both zinc and tert-butylphenol (a nonionic organic solute) show unexpected rejection at surfactant concentrations moderately below the CMC, where micelles are absent. This is considered as due to a higher surfactant concentration in the gel layer adjacent to the membrane where micelles are present. Reduction of this rejection at lower transmembrane pressure drops supports this mechanism. Some rejection of zinc was observed in the absence of surfactant but not of tert-butylphenol, indicating an additional effect of membrane charge for ionic solutes.
3.1 INTRODUCTION

In industry today, there are many potential uses for an improved, low energy separation process to remove dissolved metals or organics from water. Applications could include concentration of valuable metal products from dilute streams, or separation of toxic metals and/or organic pollutants from industrial wastewater streams. Industrial wastewaters containing dissolved metals or organics originate from many sources such as metal plating industries, metal mine-tailing leachate, coal refining, textiles and dyes manufacturing and synfuel processing. Processes that have been found most efficient in removing heavy metals or organics from aqueous streams often involve combinations of processes such as filtration, adsorption, extraction, precipitation, and distillation. These processes often require expensive reagents, are frequently energy intensive, and may still be ineffective at reducing toxin concentrations to environmentally safe levels.

Surfactant-based separation processes (1) such as micellar-enhanced ultrafiltration (MEUF) has been shown to be very effective in removing multivalent metal ions and/or organics from aqueous streams (1-14). A disadvantage of MEUF is the relatively large concentration of surfactant that must be used for an effective separation. Often, the economic viability of the MEUF process is strongly dependent on the ability to recover or recycle a substantial portion of these surfactants (15). Another option is to use small enough surfactant concentrations so recovery of the surfactant becomes less crucial from an economic point of view.
Another limitation of MEUF is the leakage of the surfactant through the ultrafiltration membrane. This can add substantial expense to the separation (7,16) or make the process effluent stream environmentally unacceptable.

An objective of this study is to investigate the use of anionic/nonionic surfactant mixtures instead of only anionic surfactants to reduce both surfactant usage and surfactant loss in MEUF for removal of metal ions or organic solutes from water.
3.2 BACKGROUND

Micellar enhanced ultrafiltration (MEUF) is a relatively low energy, pressure driven, membrane based separation process that makes use of the micellar properties of surfactant solutions to remove dissolved ions and/or organics from aqueous streams (1-14). Pressures necessary to drive MEUF range from 14 to 85 psig (97 to 587 KPa). Anisotropic membranes ranging in nominal pore size from about 10 - 100 Å (1,000 to 50,000 molecular-weight-cut-off or MWCO) are used to reject surfactant aggregates called micelles. These micelles have sequestered dissolved organics and metal ions, so these pollutants are removed with the micelles. Flux rates of pure solvent through these membranes are reported to range from approximately 0.06 - 1.0 mL/min/cm² at 60 psi (414 Kpa) transmembrane pressure drop (17).

MEUF has been used for the removal of divalent cations and/or dissolved organics from aqueous solutions. The anionic surfactant is added to the aqueous stream containing the dissolved solutes. The surfactant is present at a concentration greater than its critical micelle concentration (CMC) so that most of the surfactant is present in the micellar form (18). Micelles are surfactant aggregates that contain about 50 to 100 surfactant molecules. Divalent cations bind or absorb on the surface of the oppositely charged micelles, while organic solutes solubilize within the micelles. This solution is then passed through an ultrafiltration membrane with pore sizes small enough to block the passage of micelles. As micelles are rejected, the absorbed cations and/or solubilized organics will also be rejected. The unbound ions, unsolubilized organics and surfactant
monomers pass through the ultrafiltration membrane to the permeate side (13,14). A schematic of MEUF for ion removal is shown in Figure III. 1. A retentate-based rejection (in %) is defined as:

\[
\text{Rejection} = (100) \left(1 - \frac{[\text{solute in permeate}]}{[\text{solute in retentate}]}\right)
\]  

In MEUF, the permeate stream contains very low concentrations of the surfactant, dissolved metals or organic species. 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 and the dissolved metal/organic, and a large volume permeate stream that is relatively free of the toxins. The permeate stream can then be discarded or reused. The retentate stream is much more concentrated and considerably smaller in volume than the original process stream; therefore, further treatment or disposal of the smaller stream is less expensive.

MEUF has been shown to be very effective in removing both metals and organics from aqueous streams using surfactant concentrations much greater than the CMC. Rejections of up to 99.82% of Cu\(^{2+}\) have been reported in MEUF when using the anionic surfactant sodium dodecylsulfate (SDS) at approximately ten times its CMC (3). Comparable rejections of organics such as 4-tertbutylphenol have been accomplished using n-hexadecylpyridinium chloride (CPC) as the cationic surfactant at concentrations of CPC ranging from 40 to approximately 400 times its CMC (9,17). A divalent metal ion, in a mixture containing other metal ions, is removed with approximately the same rejection as a single metal ion under the same conditions (6). These and other previous studies have
utilized single purified surfactants, or at least single surfactant types naturally present as mixtures (e.g., mixtures of isomers or homologues) and these surfactants have been present at concentrations significantly in excess of their CMC.

Since the monomers (surfactant molecules not in micellar form) in the retentate are not substantially rejected by the ultrafiltration membrane, the total surfactant concentration in the permeate is equal to or slightly (e.g., 20%) less than the monomeric surfactant concentration in retentate or the surfactant CMC (7,9,16,17). Reducing the CMC of a surfactant results in a higher fraction of the surfactant being present as micelles. Higher micellar concentration improves the separation efficiency at a constant total surfactant concentration. In addition, reducing the CMC results in a smaller monomeric surfactant concentration in the permeate, eliminating an additional surfactant removal "polishing" step that may be required otherwise. In some cases, an extremely high rejection may not be required; by reducing the total surfactant concentration in the retentate to low enough levels, a surfactant recovery step may not be necessary.

In this paper, we will show that at a constant surfactant concentration, reducing the CMC can improve rejection by increasing the fraction of the surfactant in micellar form. The incorporation of a nonionic surfactant into micelles of ionic surfactants tends to cause separation of the charged ionic hydrophilic head groups, reducing the electrical repulsion in the Stern layer of the micelles (21-24). As the micellar surface charge density and the electrical potential at the micellar surface are reduced (24,25), less work
is required to insert an ionic surfactant into a mixed micelle than into a pure ionic micelle due to the reduced electrical repulsion. Because the mixed micelles form more easily due to the charge separation effect, the resulting CMC is lower than what would be predicted for an ideal mixed micelle. Previous studies (26-28) have shown that addition of small amounts of the nonionic surfactant, nonylphenol polyethoxylate (NPE), to the ionic surfactant SDS, results in a large decrease in the CMC value of SDS-NPE system, relative to the CMC of pure SDS. Small amounts of organic additives may also cause significant changes in the CMC of an ionic surfactant. Polar organic compounds reduce the CMC by being incorporated into micelles (16,30,31), inducing similar effects on the CMC as the nonionic surfactant. Cationic/anionic surfactant mixtures also show a very large negative deviation from ideality (18), however since these mixtures tend to precipitate or form coacervate (26) they were not investigated in this study.
3.3 EXPERIMENTAL PROCEDURES

3.3.1 Materials

Zinc chloride (ZnCl₂) (98% pure) was from Fisher Scientific. Due to the hygroscopic nature of zinc chloride, it was necessary to dry this compound at 240°C for 24 hours prior to use. The dried zinc chloride was stored in a desiccator under vacuum. The organic was 4-tertbutylphenol (TBP) (99% purity) from Aldrich and was used as received. The anionic surfactant, sodium dodecyl sulfate (SDS) (98% purity) from Fisher Scientific was purified by recrystallization from ethanol/water, followed by freeze-drying. The nonionic surfactant used was nonylphenol polyethoxylate (NPE) with an average of 10 ethylene-oxides (EO) in the hydrophilic group. This is a polydisperse commercial surfactant from Rhont-Poulenc Corp. known as IGEPAL CO-660. The NPE was used as supplied from the manufacturer. The water was treated by carbon adsorption and double ion exchanged.
3.3.2 Methods

Ultrafiltration experiments (runs) were performed using a 400 mL batch, stirred cell manufactured by Spectrum. The isothermal, isobaric process was carried out at 30°C and 60 psig (414 KPa). The temperature was maintained by circulating heated water through plastic tubing wrapped around the sleeve of the cell. High pressure nitrogen gas was used to maintain pressure. The solution in the cell was stirred using a triangular stir bar rotating at 800 RPM.

The ultrafiltration membranes, supplied by Spectrum, were composed of anisotropic cellulose acetate, with 76 mm OD, and an effective area of 38.5 cm². The molecular weight cut-off (MWCO) was 5000 Daltons. Each ultrafiltration membrane was soaked overnight in a solution containing the surfactant(s) and the multivalent counterion or organic solute at feed concentrations.

A typical ultrafiltration experiment began by pipetting 300 mL of feed solution into the cell. The run was continued until approximately 200 mL of permeate solution had been collected.

Permeate samples of approximately 15-30 mL each were collected and the concentration of dissolved material in these samples were measured; an average "midpoint" concentration for each MEUF run was then calculated. The midpoint is defined as the point at which 100 mL of permeate solution has been produced and
approximately 200 mL of retentate solution remains. The composition data reported are all midpoint unless noted otherwise.

A VARIAN AA-20 variable wavelength atomic absorption spectrophotometer was used to measure the concentration of zinc and/or sodium ions in the samples. The calibration standards were prepared by diluting zinc or sodium reference solutions (Fisher, Certified) with the surfactant. A Bausch & Lomb Spectronic 1001 variable wavelength UV absorption spectrophotometer was used to determine the NPE (wavelength 275.2 nm) or TBP (wavelength 274 nm) concentrations in the retentate and permeate samples.

A DuNoüy ring tensiometer from Central Scientific with a platinum-iridium ring was used to determine the surface tension of SDS-ZnCl₂ mixtures. A SensaDyne Model 6000 maximum bubble pressure tensiometer was used to measure the surface tension of SDS-TBP mixtures. Temperature was held constant by using a circulating water jacket around the sample while recording the measurements. For the DuNoüy tensiometer measurements, solutions were allowed to equilibrate for up to 3 hours in order to obtain accurate equilibrium surface tension readings. The CMC values were determined as the surfactant concentration at which the surface tension vs. total surfactant concentration shows a sharp change in slope.

SDS concentrations in samples were determined using a Perkin-Elmer Liquid
Chromatograph with an Alltech-320 Conductivity Detector and a Varian 4270 Integrator.
3.4 THEORY

The CMC approximates the surfactant concentration in monomer form (26); the difference between the total surfactant concentration and the CMC is approximately the surfactant concentration in micellar form, which is responsible for the separation in MEUF. In this section, determination of the CMC as well as predicted association of solutes with these micelles is discussed.

3.4.1 SDS-ZnCl$_2$-NPE System

The experimental CMC values for the SDS-ZnCl$_2$-NPE system can not be determined over the entire composition range of interest due to precipitation of Zn(DS)$_2$. Therefore, modified regular solution theory has been used to describe the monomer/micelle equilibrium in this system and to predict the mixture CMC (26).

For a binary system of anionic surfactant and a nonionic surfactant:

\[ C_M Y_{NPE} = X_{NPE} C_{MC_{NPE}} \exp(WX^2_{NPE}/RT) \]  \[ \text{[III.2]} \]
\[ C_M Y_{NaDS} = X_{NaDS} C_{MC_{NaDS}} \exp(WX^2_{NPE}/RT) \]  \[ \text{[III.3]} \]

where $C_M$ is the total monomer concentration (equivalent to the mixture CMC when the total surfactant concentration is at the CMC), $C_{MC_{NaDS}}$ and $C_{MC_{NPE}}$ are single component CMC values for the anionic surfactant (SDS) and the nonionic surfactant (NPE) respectively, $X_{NaDS}$ and $X_{NPE}$ are the surfactant-only based micellar mole fraction of each surfactant, $Y_{NaDS}$ and $Y_{NPE}$ are the surfactant-only based monomer mole fraction of each surfactant, $W$ is the interaction parameter, $R$ is the gas constant, and $T$ is the...
absolute temperature. Note that $W/RT$ is a dimensionless parameter. Equations III.2 and III.3 can be used to determine the value of $W$ from a mixed CMC value or from regression analysis on a range of mixed CMC data. These equations can be used in conjunction with mass balance equations (Equations III.4-III.7) written on a "surfactant-only" basis to determine the distribution and composition of the surfactant between the monomer and the micellar phases.

\[
Y_{\text{NPE}} = 1 - Y_{\text{NaDS}} \quad \text{[III.4]}
\]
\[
X_{\text{NPE}} = 1 - X_{\text{NaDS}} \quad \text{[III.5]}
\]
\[
Z_{\text{NaDS}} C_T = Y_{\text{NaDS}} C_M + X_{\text{NaDS}} C_{\text{MC}} \quad \text{[III.6]}
\]
\[
C_T = C_M + C_{\text{MC}} \quad \text{[III.7]}
\]

The $Z_{\text{NaDS}}$ is the surfactant-only based mole fraction of anionic surfactant in the bulk, $C_T$ is the total (anionic plus nonionic) surfactant concentration in solution, and $C_{\text{MC}}$ is the total surfactant concentration in the micellar form. Often, total surfactant concentrations and pure component CMC values are known or can be determined. For instance the CMC of an ionic surfactant is reduced by an increase in the electrolyte concentration; for SDS the CMC is related to the concentration of the unbound counterion; in this case $\text{Na}^-$ (32):

\[
\ln (\text{CMC}_{\text{NaDS}}) = A - B (\ln [\text{Na}^-]_{\text{un}}) \quad \text{[III.8]}
\]

where $\text{CMC}_{\text{NaDS}}$ is the CMC of dodecyl sulfate, $A$ and $B$ are constants, and $[\text{Na}^-]_{\text{un}}$ is the concentration of unbound $\text{Na}^-$ in solution. Over the range of $\text{Na}^-$ concentrations studied here, the CMC of the nonionic surfactant remains fairly constant (27).
Equation III.8 describes the variation in CMC of SDS with the addition of one counterion, Na⁺. Since unbound Zn²⁺ ions (which is the divalent cation used in this work) are also present in the mixture, the unbound Na⁺ and Zn²⁺ together can be translated into an "equivalent" Na⁺ concentration. For any mixture of NaDS + NaCl + ZnCl₂, there is a corresponding unbound equivalent Na⁺ concentration that results in a similar CMC_{NaDS} value in the solution without the divalent counterion (28,32).

\[
[Na]_{eq} = [Na^+]_{un} + 2[Zn^{2+}]_{un}
\]

[III.9]

\[
\ln (\text{CMC}_{NaDS}) = A - B (\ln[Na^+]_{eq})
\]

[III.10]

Similarly, the value of W/RT can be calculated from (19,27):

\[
\ln(-W/RT) = D - E \cdot (\ln[Na^+]_{eq})
\]

[III.11]

where [Na⁺]_{eq} is the equivalent unbound sodium concentration and D and E are constants which have been determined in previous study (28).

\[
K_2S^2 = [Na^+]_{un}\, P + [Zn^{2+}]_{un}\, P^2
\]

[III.12]

\[
\ln (\text{CMC}_{NaDS}) = K_1 + K_8 \ln (P)
\]

[III.13]

\[
S = \frac{[Na^+]_{un}\, P\, (S_{Na})}{\text{CMC}_{NaDS}\, P_{NaDS}} + \frac{[Zn^{2+}]_{un}\, P^2\, (S_{Zn})}{0.5 \text{CMC}_{ZnDS}\, (P_{ZnDS})^2}
\]

[III.14]

\[
K_8 = \frac{[Na^+]_{un}\, P\, (K_{8,Na})}{\text{CMC}_{NaDS}\, P_{NaDS}} + \frac{[Zn^{2+}]_{un}\, P^2\, (K_{8,Zn})}{0.5 \text{CMC}_{ZnDS}\, (P_{ZnDS})^2}
\]

[III.15]

where S is the surface charge density of the micelle, S_{Na} and S_{Zn} are the values of S in the cases in which sodium and zinc are the only counterions present in solution, P is the
electrical potential at the micelle surface; \( P_{\text{NaDS}} \) and \( P_{\text{ZnDS}} \) refer to the value of \( P \) for pure anionic surfactants (NaDS) and Zn(DS)\(^2\). \( K_g \) relates the actual to the hypothetical electrical work of introducing a molecule into the micelle, \( K_1 \) and \( K_2 \) are constants and \( \text{CMC}_{\text{ZnDS}} \) is the CMC of the pure zinc dodecylsulfate.

Values for the unbound sodium and zinc concentrations are needed in this model. The concentration of bound counterion is quantified by the fractional counterion binding, which is defined as the ratio of counterion charges in a micelle (from bound Na\(^+\) or Zn\(^{2+}\)) to the total number of monovalent anionic surfactant molecules in the micelle (24):

\[
B_{\text{Na}} = \frac{[\text{Na}^+]}{X_{\text{NaDS}}C_{\text{MIC}}} \quad [\text{III.16}]
\]

\[
B_{\text{Zn}} = 2 \frac{[\text{Zn}^{2+}]}{X_{\text{NaDS}}C_{\text{MIC}}} \quad [\text{III.17}]
\]

\[
B = B_{\text{Na}} + B_{\text{Zn}} \quad [\text{III.18}]
\]

From mass balances on the zinc and sodium:

\[
[Zn^{2+}]_t = [Zn^{2+}]_b + [Zn^{2+}]_{\text{un}} \quad [\text{III.19}]
\]

\[
[\text{Na}^+]_t = [\text{Na}^+]_b + [\text{Na}^+]_{\text{un}} = Z_{\text{NaDS}}C_T \quad [\text{III.20}]
\]

where \( B_{\text{Na}} \), \( B_{\text{Zn}} \), and \( B \) represent the fractional counterion binding of sodium, zinc, and the total fractional counterion binding on the micelle, \( [\text{Na}^+]_b \) and \( [\text{Zn}^{2+}]_b \) represent the concentrations of sodium and zinc that are bound onto the micelle, and \( [\text{Zn}^{2+}]_t \) and \( [\text{Na}^+]_t \) are the total concentrations of zinc and sodium in the solution.

For mixed micelles composed of ionic and nonionic surfactants, the fractional counterion binding decreases as the nonionic content of the micelle increases (24,25,33-
A relationship proposed by Hall and Price (33) to predict counterion binding on a mixed micelle has the form of Langmuir adsorption isotherm and is represented by:

\[ B = B^\circ \left( 1 - X_{\text{NPE}} \right) / (1 - B_\circ X_{\text{NPE}}) \]  

\[ B^\circ = B^\circ_{\text{Na}} + B^\circ_{\text{Zn}} \]

where \( B \) is the fractional counterion binding of all counterions on the mixed micelle, \( B^\circ \) is \( B \) on a pure anionic micelle; \( B^\circ_{\text{Na}} \) and \( B^\circ_{\text{Zn}} \) are \( B \) on pure anionic micelle. Given this total counterion binding, it is necessary to know the ratio between \( \text{Zn}^{2+} \) and \( \text{Na}^+ \) in the bound state. Empirically, the ratio of the fractional counterion binding of \( \text{Zn}^{2+} \) to that of \( \text{Na}^+ \) is assumed to be proportional to the ratio of their unbound concentrations:

\[ B_{\text{Zn}} / B_{\text{Na}} = K [\text{Zn}^{2+}]_\text{un} / [\text{Na}^+]_\text{un} \]

where \( K \) is a constant. Using data from a previous investigation (28) of the binding of \( \text{Ca}^{2+} \) on the same anionic/nonionic surfactant system as used here and assuming that the counterion binding behavior of the \( \text{Zn}^{2+} \) is similar to \( \text{Ca}^{2+} \) and by solving Equations III.16-III.20, a value of 44.9 is calculated for \( K \). Assuming that the binding behavior of \( \text{Zn}^{2+} \) is the same as \( \text{Ca}^{2+} \), results from a previous study of \( \text{Ca}^{2+} \) counterion binding on the SDS-NPE system used here (28) have been used to estimate values of the following parameters as shown in Table III.1: \( B^\circ_{\text{Zn}}, B^\circ_{\text{Na}}, B^\circ, K_2, K_1, S_{\text{Na}}, S_{\text{Zn}}, \text{CMC}_{\text{ZnDS}}, \text{CMC}_{\text{SDS}}, P_{\text{ZnDS}}, \text{CMC}_{\text{NPE}}, K_{\text{g,Zn}}, K_{\text{g,Na}}. \) From these parameters and the retentate compositions (\( C_T, Z_{\text{NaDS}}, [\text{Zn}^{2+}]_\text{d} \)), Equations III.2-III.23 can be solved for \( [\text{Zn}^{2+}]_\text{un}, [\text{Zn}^{2+}]_b, Y_{\text{NaDS}}, X_{\text{NaDS}}, Y_{\text{NPE}}, X_{\text{NPE}}, [\text{Na}^+]_\text{un}, [\text{Na}^+]_b, C_M, C_{\text{MB}}, P, S, K_9, \text{CMC}_{\text{NaDS}}, [\text{Na}^+]_\text{eq}, W/RT, B_{\text{Zn}}, \) and \( B_{\text{Na}}. \)
For an aqueous solution containing only SDS and ZnCl₂ an equilibrium model (6) can be used to predict permeate zinc concentration and subsequently to predicted zinc rejection using Equation III.1. Utilizing the concept of electroneutrality, Equations III.24-III.28 are solved to predict permeate zinc concentration.

\[ [Zn^{2+}]_{\text{unret}} \cdot [Cl^-]^2_{\text{ret}} = [Zn^{2+}]_{\text{per}} \cdot [Cl^-]^2_{\text{per}} \]  \hspace{1cm} \text{[III.24]}

\[ [Zn^{2+}]_{\text{unret}} \cdot [DS']^2_{\text{Mret}} = [Zn^{2+}]_{\text{per}} \cdot [DS']^2_{\text{per}} \]  \hspace{1cm} \text{[III.25]}

\[ [Na^+]_{\text{unret}} \cdot [DS']_{\text{Mret}} = [Na^+]_{\text{per}} \cdot [DS']_{\text{per}} \]  \hspace{1cm} \text{[III.26]}

\[ 2[Zn^{2+}]_{\text{p}} + [Na^+]_{\text{per}} = [Cl^-]_{\text{per}} + [DS']_{\text{per}} \]  \hspace{1cm} \text{[III.27]}

\[ [Cl^-]_{\text{ret}} = 2[ZnCl_2]_{\text{feed}} \]  \hspace{1cm} \text{[III.28]}

where \([Zn^{2+}]_{\text{unret}}\) is the retentate unbound zinc concentration, \([Cl^-]^2_{\text{ret}}\) is the retentate Cl⁻ concentration, \([DS']^2_{\text{Mret}}\) represents the monomeric dodecyl sulfate anion concentration in retentate, \([Na^+]_{\text{unret}}\) is the retentate unbound sodium concentration. The subscript "per" denotes the concentration of these species in the permeate solution. The values for \([Zn^{2+}]_{\text{unret}}, [DS']_{\text{Mret}}, [Na^+]_{\text{unret}}\) are calculated from the regular solution theory and are used in this model to predict permeate zinc concentration.

3.4.2 SDS-TBP System

The solubilization of organic solutes in micelles has been studied extensively (38-48). To quantify the solubilization of organic solutes by surfactant micelles, a solubilization equilibrium constant is defined (45):

\[ \kappa = \frac{X_{\text{org}}}{C_{\text{un}}} \]  \hspace{1cm} \text{[III.29]}
where $\kappa$ is the equilibrium constant, $X_{\text{org}}$ is the mole fraction of organic solute in the micellar phase, and $C_{\text{un}}$ is the molar concentration of unsolubilized organic solute. The dependence of $\kappa$ on the solute concentration or bounding on micelles can be represented by (45):

$$\kappa = \kappa_0 \left(1 - \beta X_{\text{org}}\right)^2 \quad \text{[III.30]}$$

Where $\kappa_0$ is the infinite dilution value of the solubilization constant and $\beta$ is an empirical constant. By definition and material balances:

$$X_{\text{org}} = \frac{C_s}{(C_s + C_{\text{mic}})} \quad \text{[III.31]}$$
$$C_{\text{org}} = C_{\text{un}} + C_s \quad \text{[III.32]}$$
$$C_T = C_M + C_{\text{mic}} \quad \text{[III.7]}$$

$C_{\text{org}}$ is the total concentration of the organic solute in the solution, $C_s$ is the concentration of the solubilized organic solute in micelles, $C_T$ is the total concentration of the anionic surfactant in the solution, $C_M$ is the measured CMC value for the SDS-TBP system for the concentration range used in this study, and $C_{\text{mic}}$ is the micellar concentration of the anionic surfactant. No nonionic surfactant was present in the experiments with TBP, so the equations are valid for SDS as the only surfactant.

The rejection of TBP can be approximated at equilibrium by assuming that the unsolubilized TBP concentration in the retentate, $C_{\text{un}}$, is equal to the total TBP concentration in the permeate. Since both solubilized and unsolubilized TBP are present in the retentate, using Equation III.1, TBP rejection can be defined as:

$$\text{Rejection} = (100) \left[1 - \frac{C_{\text{un}}}{(C_{\text{un}} + C_s)}\right] \quad \text{[III.33]}$$
Values for $C_S$, $X_{org}$, $\kappa$, $C_{MIC}$, and the Rejection can be calculated by knowing $C_T$, $C_M$, $\kappa_0$, $\beta$, $C_{un}$, and $C_{org}$ and by solving Equations III.7, and III.29-III.33.
3.5 RESULTS AND DISCUSSION

MEUF experiments were carried out with TBP (organic solute) in SDS and with zinc in SDS or SDS-NPE mixtures with the anionic surfactant concentrations ranging from moderately below to above the CMC of the surfactant.

3.5.1 TBP Rejection at Surfactant Concentrations Below the CMC

Addition of an organic solute to an anionic surfactant can often cause a reduction in the CMC of the surfactant. Therefore, accurate CMC values for the SDS-TBP system are required to determine the concentration at which micelles begin to form. Figure III.2 shows the measured CMC for pure SDS at 25°C; the experimental CMC value of 8.13 mM closely approximates the tabulated value of 8.2 mM (18). Figure III.3 shows the SDS surface tension as a function of SDS concentration at varying TBP concentrations and Figure III.4 shows CMC values obtained from Figure III.3. As expected, the CMC of SDS-TBP system decreased with the addition of TBP, varying the concentration of TBP from 0.1 mM to 2 mM, caused a reduction of 19% in the mixture CMC.

All MEUF experiments with TBP were carried out with an initial retentate (feed) TBP concentration of 2 mM. The rejection of TBP in pure water was determined to be 7%. Measurements of TBP concentration in both retentate and permeate indicated some disappearance of this solute. Since the membranes were preequilibrated in the feed solution prior to use, it was concluded that the observed small rejection is probably due to adsorption of TBP on the membrane.
Figure III.5 shows TBP rejection with SDS concentrations ranging from 0 up to 6.5 mM which is the CMC value at the TBP concentration present. At these low surfactant concentrations at which no micelles are present, no rejection of TBP was expected. However, TBP rejections ranging from 15% to 35% were measured. These rejections are too high to be caused by the adsorption effect since this value was shown to be about 7%. We propose a gel layer mechanism to explain this unanticipated rejection.

Figure III.6 shows the boundary and gel layer formation that is possible in ultrafiltration (49). The concentration of a solute species being rejected by an ultrafiltration membrane becomes higher in the region of the retentate solution adjacent to the membrane surface than in the bulk retentate solution. Generally, the flux of solvent through the membrane decreases due to an increase in the overall resistance to flow caused by the increase in rejected solute particles in the boundary layer. The true rejection of the solute is no longer a function of the solute concentration in the bulk retentate solution, but becomes a function of the solute concentration at the surface of the membrane. High shear rates near the membrane surface act to minimize the effects of concentration polarization (49) by decreasing the boundary layer thickness, but concentration polarization can still be observed. Gel polarization occurs when the concentration of solute at or near the membrane surface reaches a maximum value, commonly referred to as the gel concentration $C_g$. This concentration is independent of pressure differential across the membrane, flow conditions, and membrane characteristics (17,49). When the bulk retentate solute concentration equals $C_g$, flux becomes zero.
From the perspective of permeate rejection, the effects of the increased concentration of solute near the membrane surface have been shown to cause "presieving" that actually aids the membrane in rejecting solutes. The experiments in this work were conducted at surfactant concentrations believed to be much smaller than those at which a gel layer may form, but some level of concentration polarization is probably occurring adjacent to the membrane surface. In this small boundary layer, micelles are present to solubilize TBP or to bind to ions, resulting in a separation that cannot be explained on the basis of regular solution theory or the solubility model.

Figure III.5 also includes the predicted TBP rejections using the solubilization model. The model predicted no rejection at or below the CMC while an experimental rejection of 35% is observed. The solubilization model has been accurate in predicting solute rejections at surfactant concentrations above the CMC. However, since the model does not include corrections for concentration polarization and adsorption effects, it does not predict any rejection at or below the CMC of the system.

3.5.2 Zinc Rejection at Surfactant Concentrations Below the CMC

Figure III.7 shows that Zn$^{2+}$ rejections in water (surfactant absent) ranged from 10% to 20% with initial retentate (feed) Zn$^{2+}$ concentrations ranging from 0.25 to 30 mM. In the absence of any surfactant and with a negligible disappearance of Zn$^{2+}$ from the permeate and the retentate (insignificant zinc adsorption on the surface), the observed rejections may be attributed to the presence of the membrane charge. Previous studies by
Bhattacharyya et al. (40-53) have shown that the nature of the membrane (charged or uncharged) affects the separation of inorganic ions. Negatively charged noncellulosic membranes were shown to reject low molecular weight electrolytes in aqueous solutions due to membrane charge effect (53). For a membrane containing fixed negative sites, the anions (coions) are repelled from the membrane, and because of the requirements of electroneutrality, cations are also repelled from the solution in the membrane pores. Those studies showed that solute rejection is affected by pressure, solute concentration, anion charge density, and interaction of fixed membrane charge sites with cations. With no surfactant and with no significant Zn$^{2+}$ adsorption on the membrane, no rejection of Zn$^{2+}$ is expected; but as seen in Figure III.7, rejections were 10 to 20%. Since the cellulose acetate membranes used in this study carry a small negative charge, the "membrane charge" effect is responsible for this separation under these conditions. Furthermore, the rejection decreased with an increase in initial retentate Zn$^{2+}$ concentration, consistent with observations reported by Bhattacharyya et al.

Zinc rejections at surfactant concentrations below the CMC are shown in Figures III.8 and III.9 at approximately 1 mM and 3.4 mM retentate SDS concentrations, respectively, and with 0-0.3 mole fraction NPE (NPE concentration/total surfactant concentration). At less than approximately 5 mM retentate [SDS] and for the case of no added NPE, it is anticipated that the anionic surfactant will be present only in monomer form, but rejections of Zn$^{2+}$ ranged from approximately 46% for 1 mM retentate [SDS] to 52% for 3.4 mM retentate [SDS]. Since the membrane charge effect can only account
for 10% to 20% of this rejection, the gel layer effect is proposed to be responsible for the additional rejection.

If concentration polarization is a significant effect in MEUF at low surfactant concentrations, it is caused by a buildup of rejected species at the membrane surface and should be a function of the driving force behind the flow of solute. For MEUF, this driving force is the transmembrane pressure. It has been shown that for MEUF in batch cells, transmembrane pressures of up to 60 psi (414 kPa) can be used without causing membrane compaction effects (17). There is no added benefit to using pressures lower than this since flux rate declines as pressure decreases. A decrease in concentration polarization is expected, if the driving force for flow is decreased. This is accomplished by decreasing the pressure drop and maintaining high shear rates at the membrane surface. Figure III.10 shows the substantial decrease in Zn$^{2+}$ rejection in three identical feed solutions with the decrease in transmembrane pressure. The rejection values obtained in these experiments approach the rejections predicted by the model in the limit of 0 psi. Again, the equilibrium model does not attempt to account for membrane boundary effects, or other transient effects, this model is accurate as the flux approaches zero and the system approaches equilibrium.

3.5.3 TBP Rejection at Surfactant Concentrations Above the CMC

Figure III.11 shows TBP rejection results at above the CMC of the surfactant; the rejections of TBP ranged from 35% at SDS retentate concentration of 6.5 mM (CMC of
the system) to 94% at SDS retentate concentration of 93 mM. Comparison of rejection results at an identical initial retentate TBP concentration of 2 mM show that higher rejections of TBP are realized at higher retentate SDS concentrations. A larger fraction of surfactant is present in the micellar form at higher SDS concentration, providing more organic environment to solubilize TBP in the solution and allowing a smaller fraction of TBP to pass through the membrane to the permeate side.

The predicted TBP rejections are shown on the same Figure and closely approximate the experimental data. The solubilization model has shown to be accurate in predicting solute rejection values at above the CMC of the surfactant as shown here. However, as discussed before, the model lacks corrections for concentration polarization effects or other transient effects such as absorption. Table III.2 summarizes experimental and predicted rejection results for TBP in SDS, at surfactant concentrations ranging from below to above the CMC of SDS.

3.5.4 Zinc Rejection at Surfactant Concentrations Above the CMC

Figures III.12 and III.13 show Zn$^{2+}$ rejection at SDS concentrations of 5.9 mM and 10.4 mM, respectively and with retentate Zn$^{2+}$ concentration of 0.14 mM and NPE mole fraction of 0-0.35. Comparison of results in Figures III.12 and III.13 show that at identical retentate Zn$^{2+}$ concentrations, and without any NPE, higher rejections of Zn$^{2+}$ are realized at higher retentate SDS concentrations (99.65% vs. 99.1%). A larger fraction of surfactant is present in micelles at higher SDS concentration, providing more binding
sites for the Zn\(^{2+}\) in the solution which results in a smaller fraction of Zn\(^{2+}\) passing through the membrane to the permeate side.

Table III.3 summarizes the experimental rejections and the concentration and bulk mole fraction data obtained from the MEUF experiments along with predicted Zn\(^{2+}\) rejections, and predicted monomer and micellar mole fractions of anionic surfactant. The value for \(C_{\text{MC}}\) is predicted from the previously described regular solution model. At below the CMC, experimental rejections are higher than predicted values. One possible source of error to account for this discrepancy would be that the model under predicts the amount of surfactant in the micellar form. If this is true, more of the anionic surfactant is present as micelles and can contribute to these unexpected rejections. This is not likely, because as previously stated, regular solution theory has been found to be quite effective in predicting monomer/micelle equilibrium compositions.

Figure III.14 shows experimental Zn\(^{2+}\) rejections for the anionic/nonionic surfactant system at 54 mM retentate SDS concentration and 5.97 mM retentate Zn\(^{2+}\) concentration with NPE mole fraction ranging from 0-0.64. At these high anionic surfactant concentrations, even without added NPE, a large fraction of the surfactant is present in the micellar form (18). For the pure anionic micelle, the rejection of Zn\(^{2+}\) is 99.04%. When nonionic surfactant is first added, the rejection increases slightly as the CMC is depressed and more surfactant becomes available in the micellar form to bind to Zn\(^{2+}\). As the NPE mole fraction reaches approximately 0.2, the Zn\(^{2+}\) rejection peaks at 99.2% and
begins to decrease with further additions of nonionic surfactant. This is due to the gradual reduction in the surface charge density of the micelle as the nonionic surfactant content is increased. Even though rejection of \( \text{Zn}^{2+} \) eventually drops to 98.47% at 0.64 mole fraction NPE, this decrease in rejection is relatively insignificant and confirms that the binding ability of the anionic surfactant is not substantially effected by the fraction of the nonionic surfactant being present in the experiments.

3.5.5 Effect of Nonionic Surfactant Concentration on \( \text{Zn}^{2+} \) Rejection

It has been shown, for the SDS-NPE system, that the mixture CMC decreases very rapidly as nonionic surfactant is added to solution (27,28). As mentioned previously, much of the benefit of utilizing surfactant mixtures lies in the ability of the nonionic surfactant molecules to reduce electrostatic repulsion in the micelles. With the decreased in repulsion forces, the formation of micelles is favored at even lower surfactant concentrations leading to reduced CMC values. The CMC of this system was seen to decrease over an order of magnitude with the addition of only about 0.13 mole fraction NPE. With subsequent additions of NPE, from 0.13 up to a pure nonionic micelle, the CMC was seen to further decrease by only a factor of 2.5 (27). Therefore, small additions of the nonionic surfactant to an anionic surfactant can substantially improve metal removal. The reason lies in the unique distribution of surfactants between the monomer and micellar phases. For example in the case of the data represented in Figure III.7, the midpoint retentate contains approximately 3.4 mM SDS and 0.13 mM ZnCl\(_2\). With no added nonionic surfactant, a regular solution model of the system would predict
that conditions are below the CMC and indicate no rejection of Zn\(^{2+}\), while an experimental rejection of 52% of Zn\(^{2+}\) is observed. (26,54,55). An increase in NPE mole fraction from 0.05 to 0.23, caused an increase in rejection of Zn\(^{2+}\) from 86% to 99%. This indicates that when a small amount of nonionic surfactant is present in an anionic/nonionic system, the nonionic surfactant is incorporated to a high extent into the micelle. In fact, it is recognized that at increasing fractions of nonionic surfactant, counterion binding is eventually decreased. The space taken up by the nonionic hydrophilic groups causes a reduction in the density of the ionic hydrophilic groups on the micellar surface. This results in a reduction in the absolute surface electrical potential of the micelle (22,33,35). Electrostatic charge shielding of the ionic surfactant head groups by the ethylene oxide groups in the polyethoxylate has been seen in mixed micelles (24,25). These factors can eventually result in a reduced driving force for counter ion binding. Consequently, only a small addition of nonionic surfactant, results in higher metal removal efficiencies.

Figures III.15-III.18 represent the same experimental data that were discussed in Figures III.8, III.9, III.12, and III.13. In Figures III.15-III.18, the data are plotted as Zn\(^{2+}\) permeate concentration versus mole fraction of NPE. In one pass through a MEUF process utilizing mixed surfactants, Zn\(^{2+}\) concentration is reduced from approximately 0.12 mM in the retentate to less than 0.002 mM Zn\(^{2+}\) in the permeate. This was observed for anionic surfactant concentrations of greater than 1 mM which includes retentate SDS concentrations ranging from 3.4 mM to 10.5 mM.
3.6 CONCLUSIONS

Both Zn$^{2+}$ and TBP were rejected at SDS concentrations where theoretically no micelles exist. Higher rejections of Zn$^{2+}$ than TBP was observed at these low SDS concentrations. The observed rejection of Zn$^{2+}$ in the vicinity of the CMC of the surfactant is due to presence of concentration polarization and membrane charge effect. Concentration polarization results in the formation of micelles near the membrane surface below the surfactant CMC; concentration polarization was shown to decrease as the driving force for flow, the transmembrane pressure was decreased. Negatively charged membrane rejected Zn$^{2+}$ cations but not TBP; indicating the effect of membrane charge on the anionic surfactant and its associated cations. Zn$^{2+}$ rejections as high as 99.95% was observed for a mixed SDS-NPE system containing as little as 1.2 mM SDS. Rejections of this magnitude with anionic surfactants alone would require more than 5 times as much surfactant. Rejection of metals at these low surfactant concentration ranges is strongly dependent on anionic surfactant concentration, mixed surfactant composition, and transmembrane pressure.
3.7 REFERENCES


Table III. 1
Parameters

CMC_{SDS} = 6.652 \times 10^{-3} \text{ M}
CMC_{NPE} = 4.2 \times 10^{-3} \text{ M}
A = -8.5134
B = 0.698
D = 0.1975
E = 0.2105
K_2 = 2.87 \times 10^5 \text{ M m}^4 \text{ C}^{-2}
K_1 = -10.54
S_{Na} = 7.96 \times 10^{-3} \text{ C m}^{-2}
P_{SDS} = 2736
S_{zn} = S_{Ca} = 6.816 \times 10^{-3} \text{ C m}^{-2}
CMC_{ZnDS} = 1.9 \times 10^{-3} \text{ M}
P_{ZnDS} = P_{CaDS} = 118.52
K_{g, Na} = 0.698
K_{g, zn} = K_{g, Ca} = 0.895
K = 44.9
B^\circ = 0.65
B^\circ_{Na} = 0.45
B^\circ_{zn} = B^\circ_{Ca} = 0.2
\kappa_0 = 364 \text{ M}^{-1}
\beta = 1.14
# Table III. 2

## Experimental and Predicted TBP Rejections in MEUF

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<th>Permeate [TBP], mM</th>
<th>$X_{org}$</th>
<th>Rejection %</th>
<th>Permeate [TBP], mM</th>
<th>$C_{org}$ mM</th>
<th>$X_{org}$</th>
<th>Rejection %</th>
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Table III. 3

Summary of Experimental Zinc and SDS Concentrations, and Experimental Zinc Rejections Model Monomer/Micelle Mole Fractions and Predicted Zinc Rejections

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<th>C&lt;sub&gt;T&lt;/sub&gt;, mM</th>
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<th>Retentate [Zn&lt;sup&gt;2+&lt;/sup&gt;], mM</th>
<th>Experimental Rejection, %</th>
<th>X&lt;sub&gt;NAD&lt;/sub&gt;S</th>
<th>Y&lt;sub&gt;NAD&lt;/sub&gt;S</th>
<th>C&lt;sub&gt;mic&lt;/sub&gt;, mM</th>
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<td>7.25</td>
<td>0.9</td>
<td>0.003</td>
<td>0.296</td>
<td>98.95</td>
<td>0.742</td>
<td>0.999</td>
<td>2.808</td>
<td>84.5</td>
</tr>
</tbody>
</table>
Figure III.1 Schematic of Micellar-Enhanced Ultrafiltration
Figure III.2  Surface Tension of Pure SDS

CMC = 8.13 mM
Figure III.3 SDS CMC as a Function of [TBP]

- 0.1 mM TBP, CMC=8.06 mM
- 0.5 mM TBP, CMC=7.18 mM
- 1 mM TBP, CMC=6.65 mM
- 2 mM TBP, CMC=6.5 mM
Figure III.4 Surface Tension of SDS with Added TBP
Figure III.5 TBP Rejection vs. Retentate [SDS], Below CMC

Initial Retentate [TBP] = 2 mM

- Experimental
- Model Prediction
Skin

Well-Mixed Laminar Sub-Layer

Anisotropic Solubility Gel Layer Membrane

Figure III.6 Boundary and Gel Layer Formation in Ultrafiltration
Figure III.7  Zinc Rejection vs. Initial Retentate [Zinc] in Pure Water

Zinc Rejection, %

0  5  10  15  20  25  30

Initial Retentate [Zinc], mM

No Surfactant
Figure III.8 Zinc Rejection vs. NPE Mole Fraction

Zinc Rejection, %

Retentate [Zinc] = 0.11 mM
Retentate [SDS] = 1 mM
Figure III.9  Zinc Rejection vs. NPE Mole Fraction

Zinc Rejection, %

0 0.05 0.1 0.15 0.2 0.25 0.3
NPE Mole Fraction

Retentate [Zinc] = 0.13 mM
Retentate [SDS] = 3.4 mM
Figure III.10 Zinc Rejection as a Function of Transmembrane Pressure

- Retentate [Zinc] = 0.127 mM
- Retentate [SDS] = 4.7 mM
- Model Prediction
Figure III.11 TBP Rejection vs. Retentate [SDS], Above CMC

Initial Retentate [TBP] = 2 mM

- Experimental
- Model Prediction
Figure III.12  Zinc Rejection vs. Mole Fraction NPE

Retentate [Zinc] = 0.14 mM
Retentate [SDS] = 5.9 mM
Figure III.13 Zinc Rejection vs. Mole Fraction NPE

Zinc Rejection, %

Retentate [Zinc] = 0.14 mM
Retentate [SDS] = 10.5 mM
Figure III.14 Zinc Rejection vs. Mole Fraction NPE

Retentate [Zinc] = 5.97 mM
Retentate [SDS] = 54 mM
Figure III.15 Permeate Zinc vs. Mole Fraction NPE

Retentate [Zinc] = 0.11 mM
Retentate [SDS] = 1 mM
Figure III.16 Permeate Zinc vs. Mole Fraction NPE

Retentate [Zinc] = 0.13 mM
Retentate [SDS] = 3.4 mM
Figure III.17 Permeate Zinc vs. Mole Fraction NPE

- Retentate [Zinc] = 0.14 mM
- Retentate [SDS] = 5.9 mM
Figure III.18 Permeate Zinc vs. Mole Fraction of NPE

Retentate [Zinc] = 0.14 mM
Retentate [SDS] = 10.5 mM