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Ligand-Modified Colloid Enhanced Ultrafiltration. Use of Nitrilotriacetic Acid Derivatives for the Selective Removal of Lead from Aqueous Solution

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ABSTRACT

In ligand-modified, colloid-enhanced ultrafiltration (LM-CEUF), a ligand that selectively complexes target ions (e.g., lead) also associates with a water-soluble colloid, such as a surfactant micelle or polyelectrolyte. The colloid, associated ligand, and target ion are then concentrated using

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ultrafiltration, producing a filtrate with a low concentration of the target ion. Dialysis, ultrafiltration, and potentiometric titration experiments have been used to investigate the effectiveness of four nitrilotriacetic acid (NTA) derivatives in the removal of lead from aqueous solution through LM-CEUF. The ligands are 2-phenyl nitrilotriacetic acid (PNTA), 2-[*N,N*-di-(carboxymethyl)]amino-octanoic acid (HNTA), 2-[*N,N*-di-(carboxymethyl)]amino-dodecanoic acid (DNTA), and 2-[*N,N*-di-(carboxymethyl)]amino-3-sulfopropionic acid (SNTA). The colloids used were the cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDADMAC) and the cationic surfactant cetylpyridinium nitrate ($CPNO_3$). In equilibrium dialysis and ultrafiltration (UF) experiments, SNTA and PDADMAC systems provided effective lead removal. In semiequilibrium dialysis and UF experiments, DNTA and $CPNO_3$ systems also provided effective lead removal. The effects of pH, ionic strength, competing ions, and colloid concentration were investigated for each ligand system. Ligand protonation constants and ligand–metal stability constants were obtained for SNTA in both water and solutions of PDADMAC and for DNTA in solutions of $CPNO_3$. Ligand regeneration through pH adjustment and metal precipitation with various anions was also demonstrated.

INTRODUCTION

Colloid-enhanced ultrafiltration (CEUF) is a separation technique that can remove both organic and inorganic species from aqueous solution.[1–25] Multivalent cations, such as Pb^{2+}, can be removed through nonselective CEUF using anionic macromolecular species, such as micelles or polyelectrolytes. The metal is bound to the colloid as a result of the electrostatic attraction between the negatively charged surface of the colloid and the positively charged ion. Both the colloid and the bound metal ion are prevented from passing through the pores of the ultrafiltration (UF) membrane into the permeate stream.

An inherent problem with using conventional CEUF for the removal of metals is that there is no selectivity in the process, except on the basis of the charge of the cation; however, ligand-modified CEUF (LM-CEUF) uses derivatized chelating agents that selectively bind a target metal ion and then solubilize in or electrostatically bind to a colloidal pseudophase. Ligand-modified, micellar-enhanced ultrafiltration (LM-MEUF) requires a ligand that consists of a chelating group and a hydrophobic moiety. Such ligands are able to bind a target metal ion and then solubilize into the surfactant micelles. Ligand-modified, polyelectrolyte-enhanced ultrafiltration (LM-PEUF) utilizes multivalent anionic ligand–metal complexes that electrostatically bind to cationic polyelectrolytes. The LM-MEUF process was investigated by our group,[14–18,26] for example, using iminodiacetic acid derivatives and cetylpyridinium chloride for the removal of Cu^{2+}, and by Tondre and coworkers for divalent transition metal ions.[19–23] Tuncay et al. investigated the application of two commercially available polyprotic ligands, diethylenetriaminepentaacetic acid (DTPA) and 4,5-dihydroxy-1,3-benzenedisulfonic acid (Tiron®), for the removal of Cu^{2+} and Pb^{2-} in LM-PEUF.[24,25] In LM-CEUF, the charge of the colloid and the target ion can have the same sign; therefore, cations that are not complexed significantly by the ligand (e.g., Ca^{2+} vs. Cu^{2+}), show no rejection in the ultrafiltration. Therefore, LM-CEUF can show marked selectivity for the target ion.

Semiequilibrium dialysis (SED) and equilibrium dialysis (ED) are techniques that can be used to study the equilibrium binding and solubilization properties of colloidal systems.[27–32] Because CEUF and LM-CEUF separations, where the species to be removed from solution is retained behind the membrane, are equilibrium controlled, rather than kinetically controlled, dialysis can be used to predict the effectiveness of UF purification processes.[15,16,26,29]

We describe here results from potentiometric titration, dialysis, and ultrafiltration experiments designed to assess the applicability of nitrilotriacetic acid (NTA) derivatives in both LM-MEUF and LM-PEUF processes. NTA is known to form many metal complexes having a wide range of stabilities and high selectivity for Pb^{2+} with respect to alkaline earth cations.[33] The specific ligands investigated were 2-phenylnitrilotriacetic acid (PNTA, $C_6H_5CH(CO_2H)N(CH_2CO_2H)_2$), 2-[*N,N*-di-(carboxymethyl)]amino-octanoic acid (HNTA, $C_6H_{13}CH(CO_2H)N(CH_2CO_2H)_2$), 2-[*N,N*-di-(carboxymethyl)]amino-dodecanoic acid (DNTA, $C_{10}H_{21}CH(CO_2H)\ N(CH_2CO_2H)_2$), and 2-[*N,N*-di-(carboxymethyl)]amino-3-sulfopropionic acid (SNTA, $CH_2SO_3HCH(CO_2H)N(CH_2CO_2H)_2$). The ligands PNTA, HNTA, and DNTA were used in LM-MEUF studies with cetylpyridinium nitrate ($CPNO_3$, $CH_3(CH_2)_{15}(NC_5H_5)^+$, NO_3^-). SNTA was used in LM-PEUF studies with poly(diallyldimethylammonium chloride) (PDADMAC, $[CH_2\ (—CHCH_2N(CH_3)_2CH_2CH—)CH_2^+,\ Cl^-]_n$). Ligand protonation constants and ligand–metal stability constants were obtained for DNTA in solutions of $CPNO_3$ and for SNTA in both water and aqueous solutions of PDADMAC. The effect of experimental parameters, such as pH, ionic strength, added calcium, and colloid concentration, were investigated for each ligand system. In addition, ligand regeneration methods using pH adjustment and metal precipitation with various anions were also evaluated.

EXPERIMENTAL

Materials

Analytical reagent grade HCl, NaOH, KOH, anhydrous $Pb(NO_3)_2$, $Ca(NO_3)_2$, and $NaNO_3$ were used as received from Aldrich Chemical Co. Cetylpyridinium nitrate ($CPNO_3$) was prepared by the addition of a 10-fold excess of $NaNO_3$ to a 0.05-M solution of cetylpyridinium chloride (98% purity from Hexcel Chemical Co.), followed by filtration to recover the product. The process was repeated and the resulting solid was tested for chloride using $AgNO_3$. The chloride-free product was recrystallized four times from water.

Poly(diallyldimethylammonium chloride) (PDADMAC), 20% in water, was obtained from Aldrich Chemical Co. and was purified by removing low-molecular weight fragments through ultrafiltration using a spiral wound module with a 10,000 Da molecular weight cutoff membrane. The concentration of the resulting stock solution, expressed in terms of monomer subunits, was determined using a total organic carbon (TOC) analyzer (Dohrman Model DC-180).

The ligands PNTA and HNTA were synthesized using the general procedure described by Irving and Miles for PNTA.[34] In this procedure, chloroacetic acid, KOH, and the appropriate α-amino acid were allowed to react at room temperature for 2 weeks. The resulting solids were recrystallized four times from warm water (PNTA, HNTA) or 50:50 ethanol and water (DNTA). 2-Aminododecanoic acid, required for the synthesis of DNTA, was made using the method described by Marvel and Vigneaud for α-amino-*n*-caproic acid.[35] In this case, a slight excess ($\sim 10\%$) of 2-bromododecanoic acid (99% purity from Fluka Co.) was combined with ammonium hydroxide and the reaction was maintained at a temperature of 55°C for 2 days. The product was filtered and washed with methyl alcohol to remove ammonium bromide. 2-[*N,N*-di-(carboxymethyl)]amino-3-sulfopropionic acid (SNTA) was prepared as described by Yang.[36] Satisfactory elemental analysis (C, H, N) and ^{1}H-NMR spectra were obtained for each of the ligands.

Methods

Dialysis experiments were performed as described previously,[27–32, 37] using dialysis cells from Fisher Scientific, having 5 mL compartments separated by 6,000 Da molecular weight cutoff regenerated cellulose membranes also purchased from Fisher Scientific. These membranes were pretreated with a 0.01 M lead solution and thoroughly rinsed with deionized water. No measurable amount of lead was found to desorb when in the presence of ligand solution in the concentration range of this study. Test solutions were placed in one compartment, called the retentate, and deionized water or an electrolyte solution was placed in the other compartment, called the permeate. In all experiments, the cells were kept at 25°C for 24 hours.[3,37] ED and SED experiments were performed to study the binding and solubilization of ligand–metal complexes into colloidal pseudophases. When a polyelectrolyte is used as the colloid in ED, essentially no polymer passes through the membrane (particularly since we pretreat the polymer to remove low-molecular weight components) and the system reaches an equilibrium state. When a surfactant is used to form micelles as the colloid in SED, monomers can pass through the membrane into the permeate and slowly form micelles. If the equilibrium time is properly chosen, the total lead concentration in the permeate is approximately equal to the unbound lead concentration in the retentate. However, if equilibration time is too long, a significant fraction of the surfactant forms micelles in the permeate along with the bound counterion Pb^{2+}. In this case, a correction factor[32] needs to be applied to the measured permeate Pb concentration to calculate the unbound Pb concentrations in the retentate; hence, the term "semiequilibrium." Formal thermodynamic analysis actually requires the equality of all ion products of unassociated ions between permeate and retentate but with no added electrolyte. At the high rejections observed here, this is not necessary.[32,37] In the UF experiments described as follows, contact times across the membrane are too short for a significant concentration of micelles to form in the permeate. The efficiency of separation of a solute, X, can be evaluated in terms of rejection based on permeate ($[X]_{\text{permeate}}$) and retentate ($[X]_{\text{retentate}}$) concentrations.

$$\text{Rejection}(\%) = (100)\left(1 - \frac{[X]_{\text{permeate}}}{[X]_{\text{retentate}}}\right)$$

Ultrafiltration experiments were performed using a 400-mL stirred batch cell equipped with an ultrafilter that had a molecular weight cut-off of 5000 Da. Pressure was applied to the retentate side of the membrane using N_2 (414 kPa) to force solution through the ultrafilter. As with dialysis membranes, ultrafilters were presoaked in a 0.01 M lead solution before use. The cell was initially filled with 300 mL of solution and samples (approximately 25 mL each) were collected until 200 mL of solution had passed through the ultrafilter. When approximately 150 mL of solution had passed through the membrane, a sample of the retentate solution was removed for analysis. These "midpoint" data are tabulated in "Results and Discussion."

Potentiometric titrations were performed using a Fisher 825 pH meter and a Brinkmann Metrohm 665 Dosimat autotitration system equipped with a 5-mL buret controlled by a Zenith Z-150 PC. Titration data (pH vs. volume of titrant) was acquired using a program developed in our laboratory.[14, 38] Ligand protonation constants (K_{HL}) were obtained by analysis of the potentiometric titration data using the program PKAS.[39] This program uses an algorithm that minimizes the sum of the squares of the differences between calculated and measured pH values. Once K_{HL} values for a given ligand system were determined, potentiometric titrations were repeated for solutions containing stoichiometric amounts of ligand and Pb^{2+} or Ca^{2+}. These titration data were analyzed using the program BEST to obtain equilibrium constants for the formation of ligand–metal complexes.[40,41]

Metal concentrations in retentate and permeate samples were determined by atomic absorption spectrometry using a Varian SpectrAA20 with flame atomization or with a Varian GTA-96 graphite furnace for electrothermal atomization (for solutions with very low metal ion concentrations). To minimize the effect of interferences, the composition of standard and sample solutions were matched as closely as possible.

RESULTS AND DISCUSSION

Protonation and Complexation Equilibria

The stepwise protonation, and 1:1 metal ion-complex formation, constants for the equilibria involving nitrilotriacetic acid derivatives are defined in the following equations,

$$\mathrm{nH^+ + L^{x+} \rightleftarrows H_nL^{n-x}}$$

$$\mathrm{M^{2+} + L^{x-} \rightleftarrows ML^{2-x}}$$

$$\mathrm{K_{H_n}(n = 1 - 3,\ \ x = 3;\ \ 4(SNTA))}$$

$$\mathrm{K_{ML}}(x = 3;\ \ 4(\mathit{SNTA}))$$

The equilibrium constants for DNTA and SNTA were determined by potentiometric titration in either water or a colloid solution. Due to the low solubility of DNTA and PbDNTA in water at low pH, only titrations in the presence of colloid (i.e., 50 mM $CPNO_3$) were feasible. However, because the SNTA and SNTA-metal complexes are soluble in water, even at low pH, it was

Table 1. Summary of protonation constants for NTA derivatives.

Ligand[a]	Solution conditions	Temperature (°C)	$\log K_{H1}$[b]	$\log K_{H2}$[b]	$\log K_{H3}$	Reference
NTA	H_2O, $I = 0.1$	20.0	9.71	2.48	1.8	42
Pr-NTA	H_2O, $I = 0.1$	20.0	9.94	2.26	1.6	41
HNTA	H_2O, $I = 0.1$	20.0	10.08	2.51	1.9	41
PNTA	H_2O, $I = 0.1$	20.0	9.26	2.39	1.4	42
DNTA	0.05 M $CPNO_3$	25.0	8.97(2)	2.33(3)	<2	c
Ac-NTA	H_2O, $I = 0.1$	25.0	9.18	4.26	2.79	43
SNTA	H_2O, $I = 0.01$	25.0	8.89(2)	2.22(5)	<2	c
SNTA	0.02 M PDADMAC	25.0	8.21(8)	<2	<2	c
SNTA	0.02 M PDADMAC $+0.01$ M $NaNO_3$	25.0	8.81(7)	2.32(3)	<2	c

[a] $Pr = n\text{—}C_3H_7$, $Ac = CH_2CO_2H$.

[b] Values in parentheses give uncertainty in last decimal place.

[c] This work.

possible to obtain values of protonation and ligand–metal stability constants both in water and in solutions of PDADMAC. For each of the ligands, the value of log K_{H3} was less than 2, so reliable values were obtained for only the first two protonation steps. Values of the protonation constants for DNTA, SNTA, and several model compounds are listed in Table 1.[42–44] Two factors must be considered in explaining the observed values of the protonation and complexation equilibria; (1) effects (in H_2O) due to the added substituent, and (2) effects due to the colloidal environment. As carbon atoms are added to the alkyl chain, the values of K_{H1} increase compared to the parent compound NTA, but the increases become less pronounced after the first carbon is added.[42,43] The values of the second and third stepwise protonation constants are not substantially affected by alkyl chain length.[42,43] In the case of PNTA, the phenyl substituent causes all three protonation constants to decrease, with the largest effect noted for K_{H1}. The presence of an additional ionizable group (Ac-NTA, SNTA) results in substantial decreases in the values of K_{H1}.[43, 44] These effects are consistent with the electron withdrawing and donating and resonance properties of the substituents in question. As Table 1 indicates, the value of log K_{H1} for DNTA in 0.05 M $CPNO_3$ is significantly lower than the corresponding value for the most closely related compound (HNTA) in water, while the colloid has little effect on values of K_{H2} and K_{H3}. The value of K_{H1} for SNTA in 0.02 M PDADMAC is also less than those reported for NTA or Ac-NTA.[43,44] Table 2 summarizes

Table 2. Summary of metal ion-ligand stability constants for NTA Derivatives.

Ligand	Solution conditions	Temperature (°C)	log K_{CaL}[a]	log K_{PbL}[a]	Reference
NTA	H_2O, I = 0.1	20.0	6.41	11.39	42
Pr-NTA[b]	H_2O, I = 0.1	20.0	6.46	11.49	41
HNTA	H_2O, I = 0.1	20.0	6.47	11.29	41
PNTA	H_2O, I = 0.1	20.0	6.17	—	42
DNTA	0.05 M $CPNO_3$	25.0	4.6(2)	9.0(1)	c
SNTA	H_2O, I = 0.01	25.0	7.47(3)	11.8(3)	c
SNTA	0.02 M PDADMAC	25.0	5.46(6)	9.74(4)	c
SNTA	0.02 M PDADMAC + 0.01 M $NaNO_3$	25.0	—	11.49(3)	c

[a] Values in parentheses give uncertainty in last decimal place.
[b] Pr = n—C_3H_7.
[c] This work.

the complexation constants derived from potentiometric titrations of PNTA and SNTA with Pb^{2+} and Ca^{2-} present, along with the corresponding values for related ligands.[42,43] The complexation constants in water decrease slightly for PNTA, and are essentially unaffected by the alkyl chain substituents. On the other hand, the introduction of the methylsulfonato group results in a significant increase in the complexation constants for SNTA with Ca^{2+} and Pb^{2+}. Because sulfonate is a very weak ligand, it is likely that the change in K_{ML} is due to increased electrostatic interaction between the tetraanionic ligand and the divalent metal cation. The complexation constants of Ca^{2+} and Pb^{2+} with DNTA in $CPNO_3$ and SNTA in PDADMAC decrease by about 100-fold relative to the corresponding values in water.

The effects of micelles on acid–base equilibria have been investigated by several research groups, with shifts in the apparent protonation constants of two or more orders of magnitude reported.[45–47] Several factors have been proposed to account for these shifts. Partition of the ligand into the colloidal phase can result in the ionizable or metal complexing group being in a local environment less polar than bulk water. This would tend to increase the protonation and complexation constants relative to water, especially for oppositely charged reactants (L^{x-}/H^+, M^{2+}). This polarity factor is expected to occur to about the same extent in cationic, neutral, and anionic colloids.[47] For the cationic colloids employed in the current study, electrostatic effects must also be considered. Additional work must be done to bring the solute cation (H^+, M^{2+}) from the bulk water to the ligand bound to the positively charged colloid surface.[47] The larger shifts for the metal complexation constants ($\Delta\log K_{ML} \sim 2$) compared to the protonation constants ($\Delta\log K_{H1} < 1$) are consistent with the greater positive charge on the metal ions. The observed trends are also consistent with another explanation; the electrostatic interaction between the positively charged colloid and the cationic solutes results in lower effective concentration of H^+ or M^{2+} in the vicinity of the colloid-bound ligand.

The shifts in the protonation constant values for SNTA in 0.02 M PDADMAC are less than those obtained for DNTA in 0.05 M $CPNO_3$. One possible explanation for this is the fact that the colloid concentration was lower in the SNTA/PDADMAC titrations. Another explanation is that the electric potential at the surface of the $CPNO_3$ micelles is larger than that about the PDADMAC molecules, decreasing the effective concentration of H^+ in the vicinity of surfactant micelles. This is consistent with the results of counterion binding studies with both colloids, which show that approximately 50% of the positive charges are neutralized by Cl^- counterions in a 0.02 M PDADMAC solution[48]; whereas, the fraction of counterion binding is 70% for Cl^- in CPC micelles.[49]

The stoichiometries of ligand–lead complexes were also determined through spectrometric titration of a given ligand solution with a standardized Pb^{2+} solution. For each ligand investigated, plots of absorbance vs. total $[Pb^{2+}]$ increased linearly until the moles of Pb^{2+} added equaled the moles of ligand. At which point, the absorbance leveled off. This 1:1 stoichiometry is consistent with that determined by potentiometric titrations and found for other NTA-metal complexes in previous studies.[40,42–44]

Dialysis and Semiequilibrium Dialysis Studies

Initial SED studies were performed with PNTA, Pb^{2+}, and $CPNO_3$. As Fig. 1 indicates, the separation efficiency of Pb^{2+} is not good (rejections about 80%) with this ligand and colloid combination. It is apparent from the data that the PNTA-Pb complex stoichiometry is 1:1, because the concentration of Pb^{2+} in the permeate increases rapidly when the $[Pb^{2+}]_0$:$[PNTA]_0$ ratio exceeds unity. This is consistent with the results from potentiometric and spectrometric titrations where only 1:1 metal ion-ligand complexes were observed for NTA derivatives under the conditions employed.

Figure 2 shows that Pb rejections using PNTA and $CPNO_3$ are not affected by the presence of Ca^{2+} ions at concentrations approximately equal to the initial Pb^{2+} concentrations. This result is expected because the stability constants for NTA-Pb complexes are several orders of magnitude greater than those for NTA-Ca complexes.[42] Figure 2 also shows that $[Ca^{2+}]_{per}$ is greater than $[Ca^{2+}]_{ret}$ for all conditions studied. In this case, the cationic colloid in

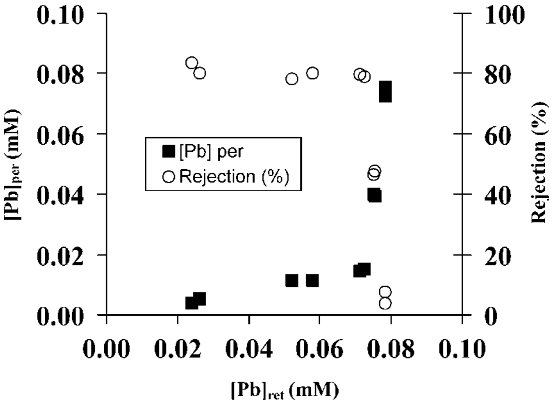

Figure 1. Effect of retentate Pb concentration on permeate Pb concentration and Pb rejection for SED experiments with 0.10 mM PNTA in 10 mM $CPNO_3$ at pH = 5.5.

the retentate causes the concentration of uncomplexed cations (Ca^{2+}) to have higher concentrations in the permeate than in the retentate. This phenomenon is known as ion-expulsion[50] and has been observed for uncomplexed species in LM-CEUF previously.[14,24,25]

The ligand HNTA was synthesized so that the ligand-Pb complex would have a large hydrophobic group and solubilize in $CPNO_3$ micelles to a greater

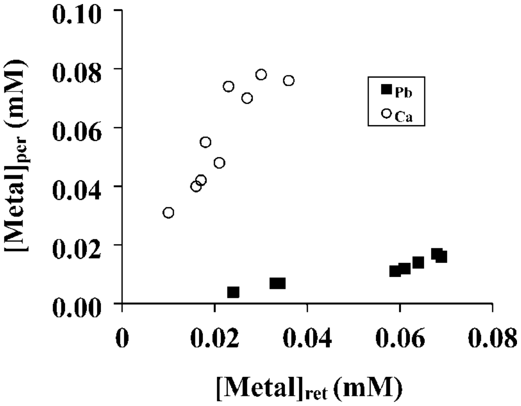

Figure 2. Effect of retentate metal concentration on permeate metal concentration for Pb and Ca mixtures ($[Pb]_0 \sim [Ca]_0$) concentrations for SED experiments with 0.10 mM PNTA in 10 mM $CPNO_3$ at pH = 5.5.

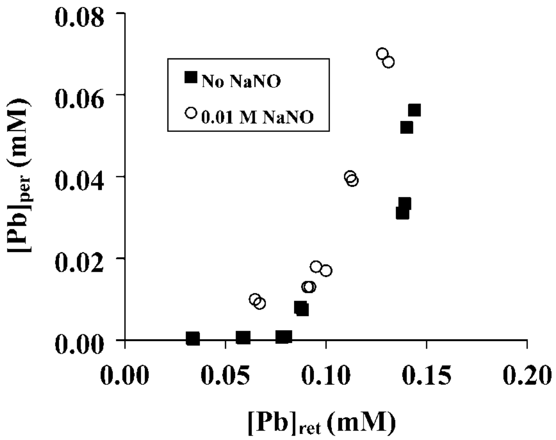

Figure 3. Effect of retentate Pb concentration on permeate Pb concentration in the absence and presence of 0.01 M $NaNO_3$ for SED experiments with 0.10 mM HNTA and Pb in 10 mM $CPNO_3$ at pH = 5.5.

extent than PNTA. Dialysis results for HNTA, Pb, and $CPNO_3$ at pH = 5.5 are depicted in Fig. 3. Because the alkyl tail imparts more hydrophobic character to the ligand-Pb complex, rejection values obtained for this system (99%) are much greater than those obtained for the analogous PNTA system (80%). The solubilization of hexane by CTAB was studied by Mahmoud et al.[51] HNTA-Pb complexes showed greater solubilization into $CPNO_3$ than hexane showed into CTAB. Although both molecules, hexane and HNTA-Pb, contain a C_6 alkyl group, the fact that HNTA-Pb can carry a net negative charge increases its partitioning into cationic micelles due to electrostatic attraction between the complex anion and the cationic surfactant head groups at the micelle surface. This effect was shown to occur in general for organic anions solubilizing into cationic micelles.[31] The role that this anionic charge plays in the solubilization of HNTA-Pb was emphasized by dialysis experiments that were performed with HNTA, Pb^{2+}, $CPNO_3$, and $NaNO_3$. As Fig. 3 shows, the presence of added salt decreases the solubilization of HNTA-Pb by reducing the electrical potential at the surface of the $CPNO_3$ micelles, reducing the electrostatic interaction between $[HNTA\text{-}Pb]^-$ and the cationic micelles. The reduced partition of HNTA-Pb into the micellar phase when $NaNO_3$ was added to the system limits the effectiveness of this ligand (rejections of $< 84\%$) in removing Pb^{2+} from water with moderate or high ionic strength. This problem can be alleviated by increasing the length of the hydrophobic carbon chain of the ligand and resultant tendency to solubilize in micelles. The four additional methylene groups present in DNTA enabled this

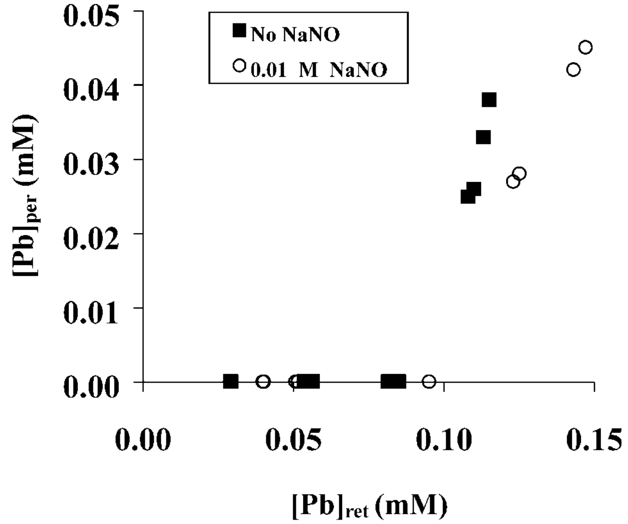

Figure 4. Effect of retentate Pb concentration on permeate Pb concentration in the absence and presence of 0.01 M $NaNO_3$ for SED experiments with 0.10 mM DNTA and Pb in 10 mM $CPNO_3$ at pH = 5.5.

ligand and its Pb^{2+} complexes to partition into $CPNO_3$ micelles to the extent that rejections greater than 99.9% were obtained, even when $NaNO_3$ was added, as shown in Fig. 4. When the $[Pb^{2+}]_0$:$[DNTA]_0$ ratio is greater than unity, the concentration of Pb^{2+} in the permeate is greater for the solutions without added $NaNO_3$ than for the corresponding solutions containing $NaNO_3$, in contrast to the results obtained for HNTA. With DNTA, the longer hydrophobic chain length may offset the decrease in the electrostatic component of partition of Pb-DNTA into the micelles observed at higher ionic strength for Pb-HNTA. On the other hand, ion expulsion effects between Pb^{2+} and the cationic micelles, which tend to increase the concentration of Pb^{2+} in the permeate, are diminished by the added electrolyte. The effect of lowering solution pH was also investigated by performing dialysis experiments with DNTA, Pb^{2+}, and $CPNO_3$ at pH 4.0. As Fig. 5 indicates, Pb^{2+} rejections were reduced when solution pH was lowered because the chelating portion of ligand was partially protonated.

Dialysis studies involving SNTA were performed in solutions of PDADMAC. The effects of solution pH, added $NaNO_3$, and added Ca^{2+} ions on Pb rejection were investigated for SNTA-Pb-PDADMAC systems. Studies were performed at solution pH values of 6.0, 5.5, 5.0, and 4.0, giving the results summarized in Fig. 6. The optimum pH was found to be between 5 and 6. For

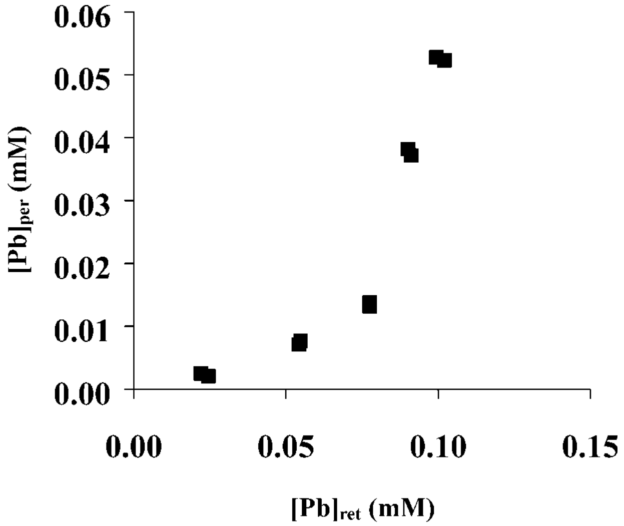

Figure 5. Effect of retentate Pb concentration on permeate Pb concentration in the absence and presence of 0.01 M $NaNO_3$ for SED experiments with 0.10 mM DNTA and Pb in 10 mM $CPNO_3$ at pH = 4.0.

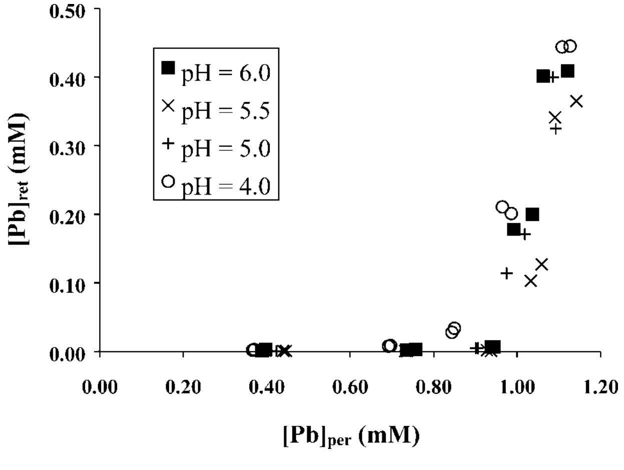

Figure 6. Effect of pH on permeateand retentate Pb concentrations from ED experiments with 1.1 mM SNTA and Pb in 20 mM PDADMAC.

example, at PDADMAC:ligand ratios of 20:1 and pH 5.5, SNTA systems had 99.9% rejection of Pb from aqueous solution. Similar rejections were obtained by Tuncay et al. for Pb^{2+} using 1,2-dihydroxy-3,5-disulfonatobenzene and diethylenetriaminepentaacetic acid as ligands in PDADMAC solutions.[24,25] The slightly poorer rejections at pH 6.0 were likely the result of $PbOH^{+}$ formation. The poorer rejections at lower pH values were likely the result of ligand protonation or perhaps Pb^{2+} desorption from the membrane surface. We did not obtain a value for the protonation constant of the SNTA-Pb complex (i.e., $[SNTA-Pb]^{2-} + \mathbf{H}^{+} \leftrightarrows [SNTA\mathbf{H} - Pb]^{-}$). Smith and Martell report a value of $\log K_{MLH} = 2.3$ for the analogous protonation reaction of NTA-Pb.[52] Considering that this value would be even lower in the presence of PDADMAC, it is unlikely that this reaction influences the SNTA systems in the pH range studied.

The rejection of lead is reduced from 99.9% to 53% as the concentration of added $NaNO_3$ increased from 0 to 0.04 M. The effect of added $NaNO_3$ on Pb distribution between permeate and retentate for the SNTA-PDADMAC

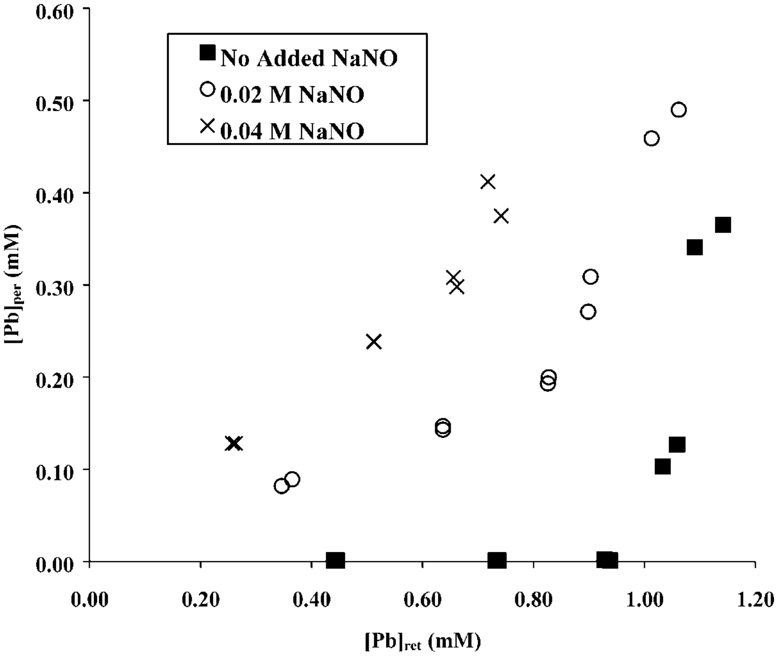

Figure 7. Effect of added $NaNO_3$ (0, 0.02, 0.04 M) on permeate and retentate Pb concentrations from ED experiments with 1.1 mM SNTA and Pb in 20 mM PDADMAC at pH = 5.5.

system is shown in Fig. 7. Experiments were performed to determine whether the lower rejection was caused by decreased binding of SNTA-Pb to PDADMAC or by increased dissociation of Pb^{2+} from colloid-bound SNTA. Evidence for the former hypotheses was obtained by TOC and AA analyses, which showed that the concentrations of SNTA and Pb^{2+} in the permeate were essentially the same (within 5%). Additional evidence for reduced SNTA-Pb binding was provided by potentiometric titrations of SNTA and SNTA with added Pb^{2+} performed in solutions containing PDADMAC and $NaNO_3$. The protonation and stability constants from these titrations (see Tables 1 and 2) were higher than those obtained in the presence of PDADMAC without added $NaNO_3$, indicating that less SNTA was in the PDADMAC pseudophase. Dialysis results for all ligand-colloid systems are summarized in Table 3. ED experiments similar to those carried out with PNTA (see Fig. 2) showed that the presence of equilimolar Ca^{2+} in the initial retentate solution had essentially no effect on Pb rejection for solutions where $[Pb^{2+}]_0$:$[SNTA]_0 < 1.0$. Under these conditions, Pb rejection was greater than 99.1%.

Ultrafiltration Studies

Ultrafiltration runs were performed for systems that exhibited excellent rejections (>99%) in dialysis experiments. Results for SNTA systems are presented in Table 4. Rejections obtained in UF experiments agree well with those obtained in ED experiments. For a system containing SNTA, Pb^{2+}, and PDADMAC at pH 5.5, a Pb rejection of 99.92% was obtained. In the presence of an equal initial concentration of Ca^{2+} ions ($[Pb^{2+}]_0 \approx [Ca^{2+}]_0$), a Pb

Table 3. Rejection of Pb^{2+} obtained by dialysis experiments at an initial ligand-metal ratio of 1:1 and pH = 5.5.

Ligand[a]	[Colloid]	$[NaNO_3]$ Added	Rejection(%)
PNTA	0.01 M $CPNO_3$	—	80
HNTA	0.01 M $CPNO_3$	—	99.0
HNTA	0.01 M $CPNO_3$	0.01 M	84
DNTA	0.01 M $CPNO_3$	—	99.96
DNTA	0.01 M $CPNO_3$	0.01 M	99.92
SNTA	0.02 M PDADMAC	—	99.91
SNTA	0.02 M PDADMAC	0.02 M	77
SNTA	0.02 M PDADMAC	0.04 M	53

[a] [PNTA] = [HNTA] = [DNTA] = 0.1 mM; [SNTA] = 1 mM.

Table 4. Ultrafiltration results for SNTA with Pb^{2+} and Ca^{2+} in PDADMAC at $pH = 5.5$.[a,b]

$[SNTA]_0$	$[Pb]_0$	$[Ca]_0$	$[Pb]_{ret}$	$[Pb]_{per}$	Rejection(%)
0.501	0.462	—	0.873	0.0011	99.92
0.519	0.471	0.511	0.889	0.0086	99.0
0.500	0.451	5.01	0.664	0.171	74.2
0.0511	0.0458	0.502	0.0891	0.0007	99.2

[a] All concentrations are expressed as mM. Subscripts are defined as 0: the initial concentration of Pb^{2+} in the retentate; ret : retentate; per: permeate.
[b] $[PDADMAC]_0 = 10\,mM$.

rejection of 99.0% was obtained; however, for the system initially containing 0.5 mM SNTA and Pb^{2+} with 5 mM Ca^{2+} in 0.01 M PDADMAC, a Pb rejection of 74.2% was obtained. This low rejection is probably not the result of increased competition for SNTA by the Ca^{2+} ions but, rather, the result of the increased ionic strength (~ 15 mM) due to the presence of the dissociated $CaCl_2$. In fact, the 74.2% rejection value agrees well with the 76% rejection values obtained for ED experiments performed with SNTA, Pb^{2+}, and PDADMAC in the presence of 0.02 M $NaNO_3$. Also, when the initial concentrations of SNTA, Pb, and Ca are reduced by a factor of ten (still keeping Ca and Pb ratio at 10:1), reducing the concentration of ions from the Ca salt by a factor of ten, a rejection of 99.2% was obtained.

The results of UF experiments performed using DNTA systems are summarized in Table 5. As the rejection values indicate, DNTA in $CPNO_3$ was effective for the removal of lead, even in the presence of large excesses of Ca^{2+} ions or $NaNO_3$. Although the added salt would reduce electrostatic

Table 5. Ultrafiltration results for DNTA with Pb^{2+} in $CPNO_3$ at $pH = 5.5$.[a,b]

$[DNTA]_0$	$[NaNO_3]_0$	$[Pb]_0$	$[Ca]_0$	$[Pb]_{ret}$	$[Pb]_{per}$	Rejection(%)
0.0500	—	0.0451	—	0.0901	<0.0001	99.93
0.0505	—	0.0449	0.0500	0.0872	<0.0001	99.91
0.0509	—	0.0473	0.504	0.0910	0.0003	99.7
0.0514	5.10	0.0461	—	0.0883	0.0002	99.80
0.0502	49.86	0.0412	—	0.0804	0.0004	99.5

[a] All concentrations are expressed as mM. Subscripts are defined as 0: the initial concentration of Pb^{2+} in the retentate; ret : retentate; per: permeate.
[b] $[CPNO_3]_0 = 0.01\,M$.

interactions between cationic micelles and anionic ligand–metal complexes, it would also reduce the interactions between head groups of surfactant monomers. The resulting surfactant aggregates have been shown to provide better solubilization results for hydrophobic solute species.[53,54]

Ligand Regeneration

To make LM-CEUF processes more economically viable in wastewater remediation, methods must be developed to regenerate and recycle the ligands and/or colloid. A regeneration method was investigated that consisted of lowering the solution pH to increase the extent of complex dissociation, followed by addition of an anionic solute to precipitate the lead. The metal ion separation achieved by the LM-CEUF process allows relatively nonselective precipitating agents such as sulfate, chromate, and oxalate to be used. The effects of pH and anionic solute concentration were examined for these precipitating agents. After precipitation, the amount of lead-free ligand remaining in solution was determined by spectrometric titration. The results for DNTA, shown in Table 6, indicate that oxalic acid provided the best results

Table 6. DNTA regeneration results using anionic solutes to precipitate Pb^{2+}.[a,b]

Anionic species	$[\text{Anion}]_0$	pH	Fraction of ligand recovered(%)[c]
$SO_4{}^{2-}$	1.02	3.02	5.1
$SO_4{}^{2-}$	1.03	2.05	27.1
$CrO_4{}^{2-}$	1.00	4.07	0.0
$CrO_4{}^{2-}$	1.05	3.10	0.0
$C_2O_4{}^{2-}$	1.00	2.06	54.6
$C_2O_4{}^{2-}$	1.03	2.51	79.4
$C_2O_4{}^{2-}$	1.07	3.00	82.8
$C_2O_4{}^{2-}$	1.01	3.52	85.8
$C_2O_4{}^{2-}$	1.08	4.01	62.8
$C_2O_4{}^{2-}$	0.50	3.50	80.1
$C_2O_4{}^{2-}$	0.24	3.52	69.2
$C_2O_4{}^{2-}$	0.10	3.50	32.4

[a] All concentrations are expressed as mM. The subscript is defined as 0: the initial concentration of anionic solute added.

[b] $[CPNO_3] = 0.01\,M$; $[DNTA] = 0.1\,mM$; $[Pb]_0 = 0.1\,mM$.

[c] % DNTA regenerated $= 100[1-([Pb]_{\text{remaining}}/[Pb]_0)]$.

Table 7. SNTA regeneration results using oxalic acid to precipitate Pb^{2+}.[a,b]

$[\text{Oxalic acid}]_0$	pH	Fraction of ligand recovered (%)[c]
1.02	3.52	39.2
2.03	3.51	89.8
4.98	3.49	96.3

[a] All concentrations are expressed as mM. The subscript is defined as 0: the initial concentration of anionic solute added.
[b] $[\text{SNTA}] = 1.0\,\text{mM}$; $[\text{Pb}]_0 = 1.0\,\text{mM}$.
[c] % SNTA regenerated $= 100[1 - ([\text{Pb}]_{\text{remaining}}/[\text{Pb}]_0)]$.

for the anionic species studied. Although the K_{sp} of $PbCrO_4$ is orders of magnitude lower than the K_{sp} of PbC_2O_4, the pH values required to cause dissociation of the ligand–metal complex (pH < 4.0) are in the range where the predominate chromate species is $HCrO_4^-$ ($pK_a = 6.49$).[55] The optimum pH for the regeneration method with oxalate was found to be approximately 3.5, where a sufficient fraction of oxalic acid is in the unprotonated form and is able to precipitate most of the Pb^{2+}available. Similar results were obtained for regeneration of SNTA using oxalate. Table 7 shows that ligand recoveries as high as 96.3% could be realized with oxalate at pH 3.5.

CONCLUSIONS

Four NTA derivatives were synthesized for use in both surfactant micelle and polyelectrolyte systems. From potentiometric titration information, it is apparent that DNTA and SNTA form stable complexes with Pb^{2+}. These stability constants are several orders of magnitude greater than stability constants obtained for the corresponding Ca^{2+} complexes, indicating that Pb^{2+} ions can be selectively complexed by NTA derivatives in solutions containing both Pb^{2+} and Ca^{2+}. This selectivity was also demonstrated in dialysis experiments involving NTA derivatives in solution with Pb^{2+} and Ca^{2+} ions. Greater than 99.9% rejection of Pb was exhibited by DNTA and 0.01 M $CPNO_3$ systems, even at elevated $NaNO_3$ concentrations. The decyl tail of DNTA had sufficient hydrophobic character to result in high solubilization of DNTA-Pb at high ionic strength. Greater than 99.9% rejections of Pb were also exhibited by SNTA and 0.02 M PDADMAC systems with no added salt; however, the rejection values dropped substantially with the addition of $NaNO_3$. Oxalic acid combined with pH adjustment was found to be effective in the regeneration of up to 86% DNTA and 96% SNTA from systems containing ligand, Pb^{2+}, and colloid.

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