Ligand-Modified Polyelectrolyte-Enhanced Ultra-filtration: Use of Carbonate and 1,2-Dihydroxy-3,5-benzenedisulfonic Acid to Remove UO_2^{2+} from Aqueous Solutions.

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Project Title: Removal of Radioactive Cations and Anions from Polluted Water Using Ligand-Modified Colloid-Enhanced Ultrafiltration.
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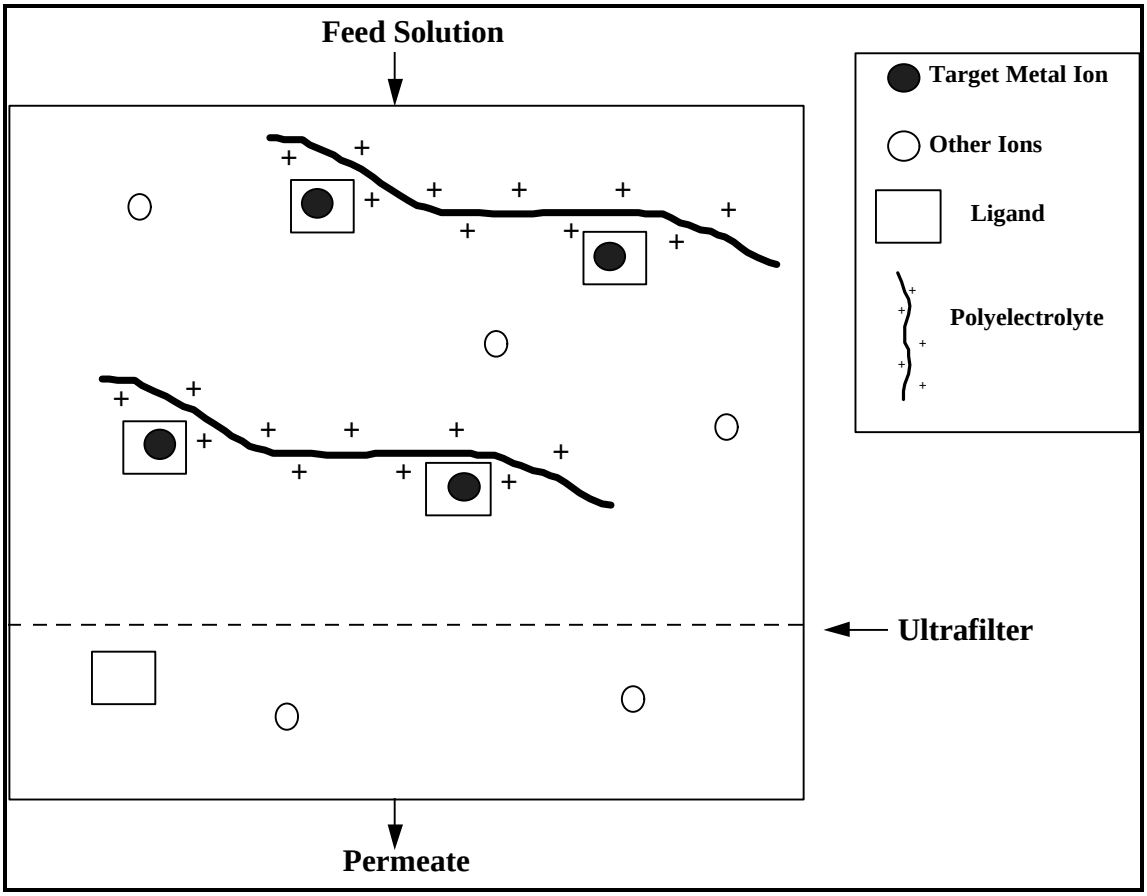
ABSTRACT: Ligand modified-colloid enhanced ultrafiltration is a membrane-based separation method where a surfactant or soluble polymer and a complexing agent are added to a metal-ion contaminated waste stream. The mixture is then forced through a membrane with sufficiently small pore sizes to reject the colloid and the attached metal complex species producing a purified permeate and concentrating the pollutants in the retentate. Equilibrium dialysis and stirred-cell ultrafiltration methods have been used to investigate the effectiveness of the anionic ligands carbonate and 4,5-dihydroxy-1,3-benzenedisulfonic acid (DHBDSA) for removal of uranyl cation (UO_2^{2+}) from aqueous solution. The cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDADMAC) was used as the colloid. Complexes formed by UO_2^{2+} with these ligands have a net anionic charge and are thus retained by the cationic polymer through electrostatic interaction. For solutions initially containing 0.13-0.96 mM uranyl cation, equilibrium dialysis experiments gave UO_2^{2+} rejections in the range 99.38%-99.98% and 99.68%-99.95% for the carbonate- and DHBDSA-PDADMAC systems, respectively. Ultrafiltration studies under similar conditions gave UO_2^{2+} rejections in the range 98.17%-99.98% and 99.82%-99.94% for carbonate and DHBDSA ligands, respectively. The effects of experimental parameters including UO_2^{2+} concentration, ligand concentration, pH, added electrolyte (NaCl), and colloid concentration were investigated.

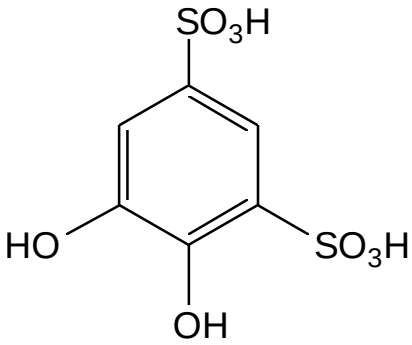
INTRODUCTION: The objectives of this project are to evaluate the feasibility of, and to determine the optimum conditions for the use of colloid-enhanced ultrafiltration (CEUF) methods to remove and recover radionuclides and associated toxic non-radioactive contaminants from polluted water. The target metal ions are uranium, plutonium, thorium, strontium and lead, along with chromium (as chromate). Separation and concentration of the target ions will result in a substantial reduction in the volume of material requiring long-term storage or further treatment.

Ligand-modified polyelectrolyte-enhanced ultrafiltration (LM-PEUF) is a membrane-based separation method where a soluble cationic polymer and a anionic complexing agent are added to a metal-ion contaminated waste stream (1-5). If the metal ion complexes formed have a net anionic charge they will be retained by the cationic polymer through electrostatic interaction. The mixture is then forced through a membrane with sufficiently small pore sizes to reject the polymer and the attached metal complex species producing a purified permeate and concentrating the pollutants in the retentate. The process is illustrated in the schematic diagram shown below.

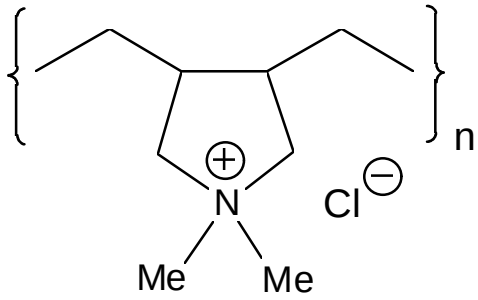


Schematic diagram of system for ligand-modified polyelectrolyte-enhanced ultrafiltration (LM-PEUF)

For the studies reported here, UO_2^{2+} is the target cation, the ligands are 4,5-dihydroxy-1,3-benzenedisulfonic acid (DHBDSA) and carbonate (CO_3^{2-}), and the soluble cationic polyelectrolyte is poly(diallyldimethylammonium chloride) (PDADMAC).



DHBMSA



PDADMAC

UO_2^{2+} forms a variety of anionic complexes with carbonate and ternary hydroxy-complexes defined by the reactions (6);

$$x\,UO_2^{2+} + y\,CO_3^{2-} \leftrightarrow (UO_2)_x(CO_3)_y^{2x-2y} \quad (x = 1, 3;\ y = 1\text{-}3, 6)$$

$$x\,UO_2^{2+} + y\,CO_3^{2-} + z\,OH^- \leftrightarrow (UO_2)_x(CO_3)_y\,OH)_z^{2x-2y-z}$$
$$(x = 1, 2;\ y = 1;\ z = 1, 3)$$

as well as mono- and polynuclear (cationic) hydrolysis products;

$$x\,UO_2^{2+} + z\,OH^- \leftrightarrow (UO_2)_x(OH)_z^{2x-z} + z\,H^+ \quad (x = 1\text{-}4;\ z = 1\text{-}7)$$

DHBDSA (L) forms primarily 1:1 and 3:3 hydroxy-complexes (7);

$$UO_2^{2+} + L^{4-} \leftrightarrow UO_2\,(L)^{2-} + 2H^+$$
$$3\,UO_2^{2+} + 3L^{4-} \leftrightarrow (UO_2)_3(OH)_2(L)_3^{8-} + 2H^+$$

The effects of experimental parameters including UO_2^{2+} concentration, and ligand concentration, pH, added electrolyte (NaCl), and colloid concentration were investigated. Equilibrium dialysis (ED) and stirred-cell ultrafiltration (UF) were the methods used to evaluate the potential of these systems for UO_2^{2+} separations by LM-PEUF. The degree of retention of the target ion UO_2^{2+} is expressed as a rejection coefficient, R_{UO2}(%),

$$R_{UO2}(\%) = \{ 1 - [UO_2^{2+}]_{per} / [UO_2^{2+}]_{ret} \} \times 100\% \qquad (1)$$

where $[UO_2^{2+}]_{per}$ and $[UO_2^{2+}]_{ret}$ refer the to the concentrations of UO_2^{2+} in the permeate (filtrate) and retentate (retained) solutions, respectively.

MATERIALS AND METHODS

Chemicals: Analytical reagent grade Na_2CO_3 , $NaHCO_3$, Arsenazo III, NaCl, 4,5-dihydroxy-1,3-benzenedisulfonic acid (DHBDSA), and $U^{IV}O_2(NO_3)_2 \cdot 6H_2O$ (purity 99+%) were used as received. PDADMAC was obtained as a 40% solution in water and purified by ultrafiltration using a 10K MWCO cellulose acetate membrane. The concentration of PDADMAC in the purified solution was determined using a total carbon analyzer.

Analysis of test solutions: UO_2^{2+} concentrations were measured using a colorimetric method based on the reaction of Arsenazo III with UO_2^{2+} in 5.6 M $HClO_4$ (8). Absorbance measurements at 656 nm gave linear calibration curves with a detection limit of ~0.0005 micromoles of UO_2^{2+} (~0.1 μM UO_2^{2+}), rel. error in this range ~ 6%. DHBDSA concentrations were determined by direct spectrophotometric measurements.

Equilibrium Dialysis Experiments: Dialysis experiments used cells with ~5 mL compartments separated by a 6000 MWCO regenerated cellulose acetate (RCA) membranes. The test solution (polymer, UO_2^{2+}, ligand, salt) was placed in the retentate side and pure water, or a solution containing the desired electrolytes was placed in the permeate compartment. The cells were maintained at 25° C for 24-48 hours before analysis (9).

Ultrafiltration Experiments: Ultrafiltration experiments were performed at room temperature using a 400 mL stirred cell at an applied pressure (60 psig) equipped with a 10,000 MWCO RCA membrane (10). Samples (250 mL) of the test solution (polymer, UO_2^{2+}, ligand, salt) were introduced as the feed. and about 200 mL of the solution was filtered. The first 10 mL was discarded and portions of ~ 25 mL each were collected for analysis.

Equilibrium dialysis results the UO_2^{2+} - carbonate system: Effect of absence of PDADMAC and/or $[CO_3^{2-}]_0$ (i.e., blanks)

$[UO_2^{2+}]_0$ = 0.66 mM, pH 7.5

PDADMAC (mM)	$[CO_3^{2-}]_0$ (mM)	$[UO_2^{2+}]_{ret}$ (mM)	$[UO_2^{2+}]_{per}$ (mM)	R_{UO2} [a] (%)	(E_{UO2}) [b] (%)
0.0	0.0	0.281	0.280	0.0	(0.0)
11.65	0.0	0.058	0.540	- - -	(89.3)
0.0	3.00	0.318	0.214	32.7	(- - -)

[a]Rejection (%): $R_{UO2} = (1 - [UO_2^{2+}]_{per} / [UO_2^{2+}]_{ret}) \times 100\%$

[b]Expulsion (%): $E_{UO2} = (1 - [UO_2^{2+}]_{ret} / [UO_2^{2+}]_{per}) \times 100\%$

The data listed above illustrate aspects of the behavior of the UO_2^{2+} - carbonate-PDADMAC system in dialysis experiments. The first entry (no polymer, no carbonate) shows the expected equal concentrations of UO_2^{2+} in the permeate and retentate, indicating that membrane adsorption of the cation is negligible. The second entry (no carbonate) shows that electrostatic interaction between the cationic polymer and UO_2^{2+}, results in substantial expulsion of the UO_2^{2+} into the permeate (10). This phenomenon could be exploited in stripping / recovery steps following the initial separation. The third entry (no polymer) shows a modest rejection of UO_2^{2+}, possibly due to membrane interactions with anionic uranyl-carbonate(-hydroxy) complexes.

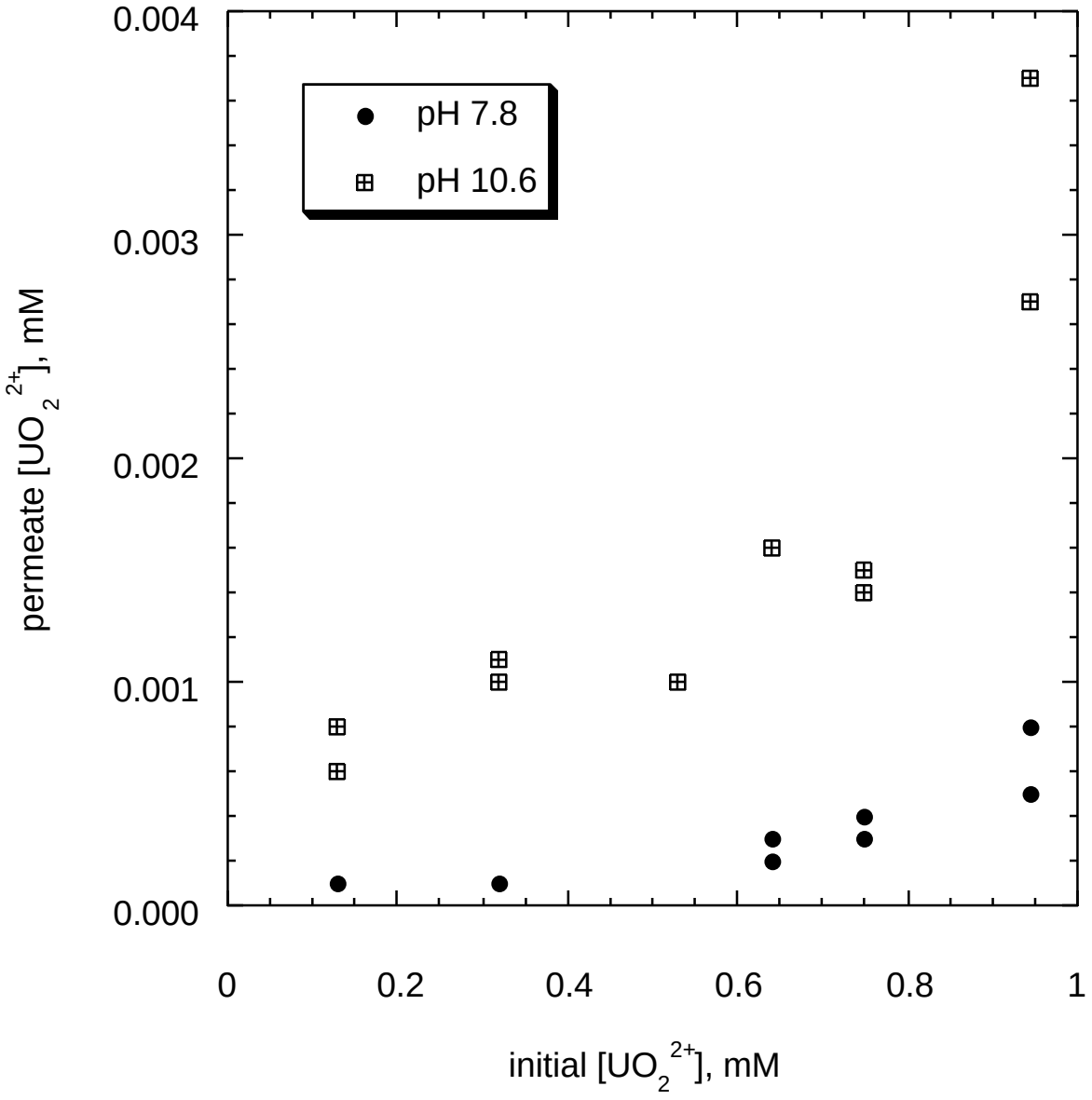
Equilibrium dialysis studies: UO_2^{2+} - CO_3^{2-} - PDADMAC.

The following two panels show the results of ED studies on the UO_2^{2+} - CO_3^{2-} - PDADMAC system. The effects of initial UO_2^{2+} concentration (0.13-0.96 mM), pH (7.8 - 10.6), and added electrolyte (NaCl) on the rejection of UO_2^{2+} were investigated. Applying equation **1** to the data in the first figure gives UO_2^{2+} rejection values in the range 99.91-99.98% at pH ~7.8. The range of rejections decreases slightly, to 99.38-99.82%, at pH ~10.6. The modest decrease in R_{UO2} at higher pH may be a consequence of a shift in the complexation equilibria favoring monoanionic ternary hydroxy species such as $(UO_2)_xCO_3(OH)_z^-$ at the expense of the more tightly bound polyvalent $UO_2(CO_3)_z^{2-2z}$ complexes.

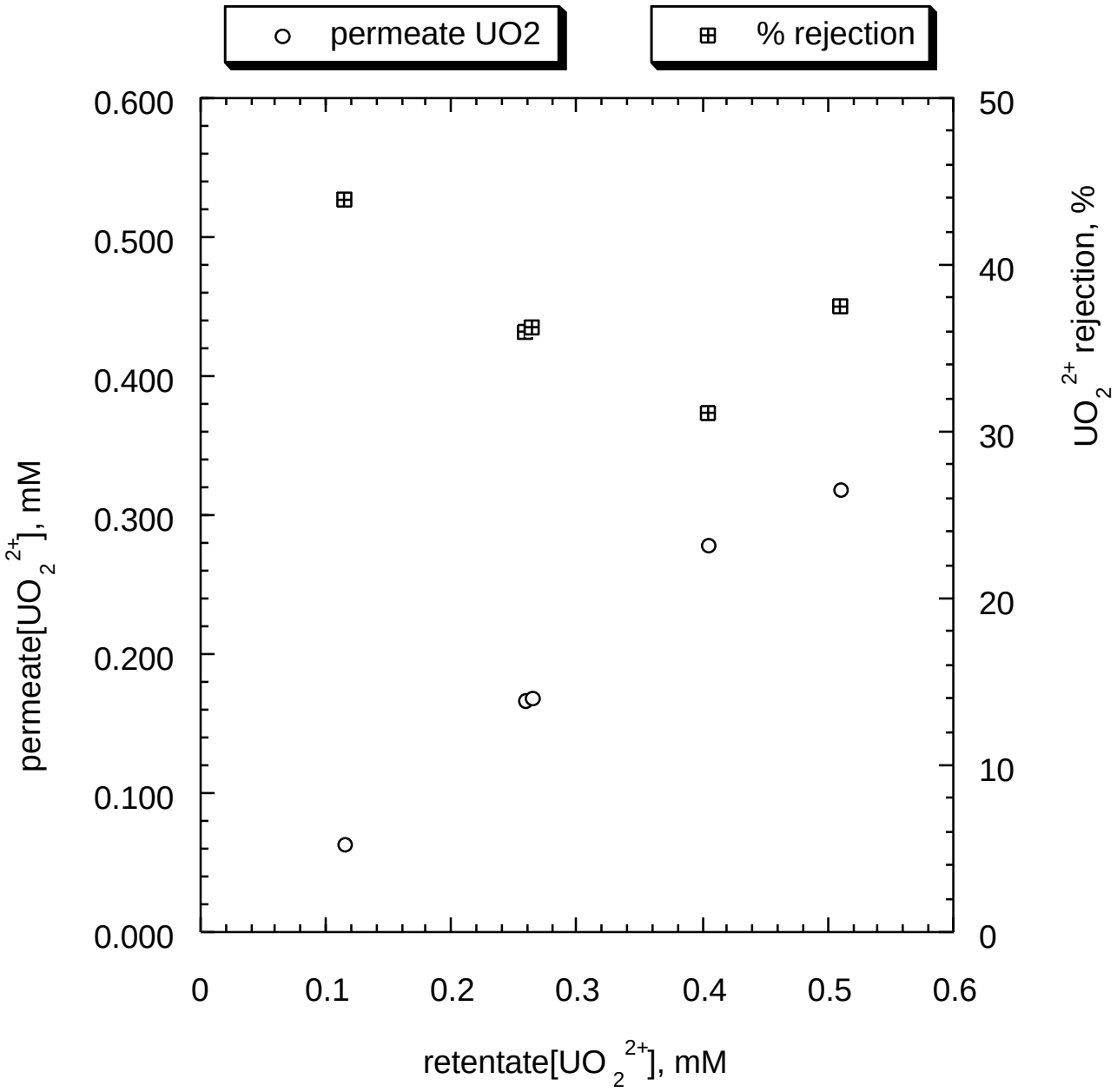
The second plot shows that increased ionic strength, due to added NaCl (0.2 M), causes a substantial decrease in R_{UO2} at pH ~8; from ≥ 99.9% to 31-45%. The increased ionic strength alters the uranyl complexation equilibria involving charged reactants and, more importantly, diminishes the electrostatic interaction responsible for the binding/attachment of the anionic uranyl complexes to the cationic polymer.

Although this effect may limit the use of carbonate as a ligand for LM-PEUF at high salt concentrations, this behavior may be exploited in developing strategies for UO_2^{2+} stripping and polymer recovery.

Equilibrium dialysis results for UO_2^{2+} - CO_3^{2-} - PDADMAC: Effect of initial [UO_2^{2+}] and pH on [UO_2^{2+}] in the premeate; (Total carbonate = 10.0 mM, PDADMAC = 11.65 mM).



Equilibrium dialysis results with UO_2^{2+} and carbonate in the presence of added electrolyte, 0.2 M NaCl; (pH = 8.2, PDADMAC = 11.65 mM).



Equilibrium dialysis results the UO_2^{2+} - carbonate system: Use of low pH for stripping UO_2^{2+} and recovery of polymer.

At low pH the anionic UO_2-CO_3 and UO_2CO_3-OH complexes dissociate, giving UO_2^{2+} and H_2CO_3 (H_2O, CO_2). The data shown below indicate the feasibility of this approach to remove (strip) UO_2^{2+} and recover the polymer for re-use. At pH 7.4, 99.64% of the UO_2^{2+} is rejected by the membrane; however, when the pH is decreased to 2.3 there is net expulsion (%E_{UO2}) of UO_2^{2+} into the permeate. The degree of expulsion is diminished compared to the blank experiment at pH 7.4 (see previous Table). Most likely, this is a result of the higher ionic strength in the low pH experiment due to added HCl, and Na^+ from the initial $NaHCO_3$ / Na_2CO_3 present.

$[UO_2^{2+}]_0$ = 0.96 mM, PDADMAC = 11.65 mM

pH	$[CO_3^{2-}]_0$ (mM)	$[UO_2^{2+}]_{ret}$ (mM)	$[UO_2^{2+}]_{per}$ (mM)	R_{UO2} [a] (%)	(E_{UO2}) [b] (%)
10.55	10.0	0.880	0.0032	99.64	- - -
0.964	0.0006	99.94	- - -		
2.30	9.0	0.500	0.624	- - -	(19.9)

7.40 10.0

[a]Rejection (%): $R_{UO2} = (1 - [UO_2^{2+}]_{per} / [UO_2^{2+}]_{ret}) \times 100\%$

[b]Expulsion (%): $E_{UO2} = (1 - [UO_2^{2+}]_{ret} / [UO_2^{2+}]_{per}) \times 100\%$

Ultrafiltration Results with UO_2^{2+} and Carbonate.

A series of ultrafiltration runs were carried out based on the results of the ED experiments. The effects of varying $[CO_3]_{tot}$, [NaCl], [PDADMAC, and pH were investigated. The results are presented in the table below. In most cases the UF results parallel those obtained in from the ED experiments. Uranyl rejections were ≥ 99.9% for conditions where $[CO_3]:[UO_2] \geq 4.0$, pH ≥ 5 and there was no added salt. R_{UO2} decreased in the presence of 0.2 M - 0.5 M NaCl but not to the extent found in the ED experiments. This difference between UF and ED has been noted previously and was attributed to (flux-dependent) concentration polarization / membrane charge effects found in UF (10). The third set of entries indicate that the effect of added salt is mitigated to some extent by increased polymer concentration. Uranyl rejection varies only slightly (99.62-99.80%) in the pH range 7.6 - 10.5, but decreases considerably (74.74%) at pH 2.6. The non-zero uranyl rejection for UF at low pH also arises from charge polarization/flux phenomena. The effect of applied pressure on this behavior is currently under investigated.

Ultrafiltration Results with UO_2^{2+} and Carbonate: Effects of [PDADMAC], [NaCl], $[CO_3]_{Tot}$, and pH on rejection of UO_2^{2+}.

$[UO_2^{2+}]_0$ = 0.25 mM (parameter varied in boldface type)

PDADMAC (mM)	[NaCl] (M)	$[CO_3]_{Tot}$ (mM)	pH	$[UO_2^{2+}]_{per}$ [a] (mM)	R_{UO2} [b] (%)
5.0	0.0	**0.25**	5.00	0.0373	95.47
5.0	0.0	**1.00**	6.75	0.0002	99.96
5.0	0.0	**2.00**	6.75	0.0001	99.98
5.0	0.0	**2.50**	6.75	0.0002	99.96
5.0	**0.0**	2.50	6.75	0.0002	99.96
5.0	**0.2**	2.50	6.84	0.0273	95.97
5.0	**0.5**	2.50	6.84	0.0660	82.07
5.0	0.2	2.50	6.84	0.0273	95.97
20.0	0.2	2.50	6.72	0.0102	98.17
5.0	0.0	10.00	**7.60**	0.0010	99.72
5.0	0.0	10.00	**8.80**	0.0007	99.80
5.0	0.0	10.00	**10.50**	0.0016	99.62
5.0	0.0	2.50	**2.60**	0.1201	74.74

[a] Average $[UO_2^{2+}]_{per}$ for all fractions in an ultrafiltration run.

[b] Average % rejection for all fractions in an ultrafiltration run:

$$R_{UO2} = (1 - [UO_2^{2+}]_{per} / [UO_2^{2+}]_{ret}) \times 100\%$$

Results for the UO_2^{2+} - DHBDSA - PDADMAC System

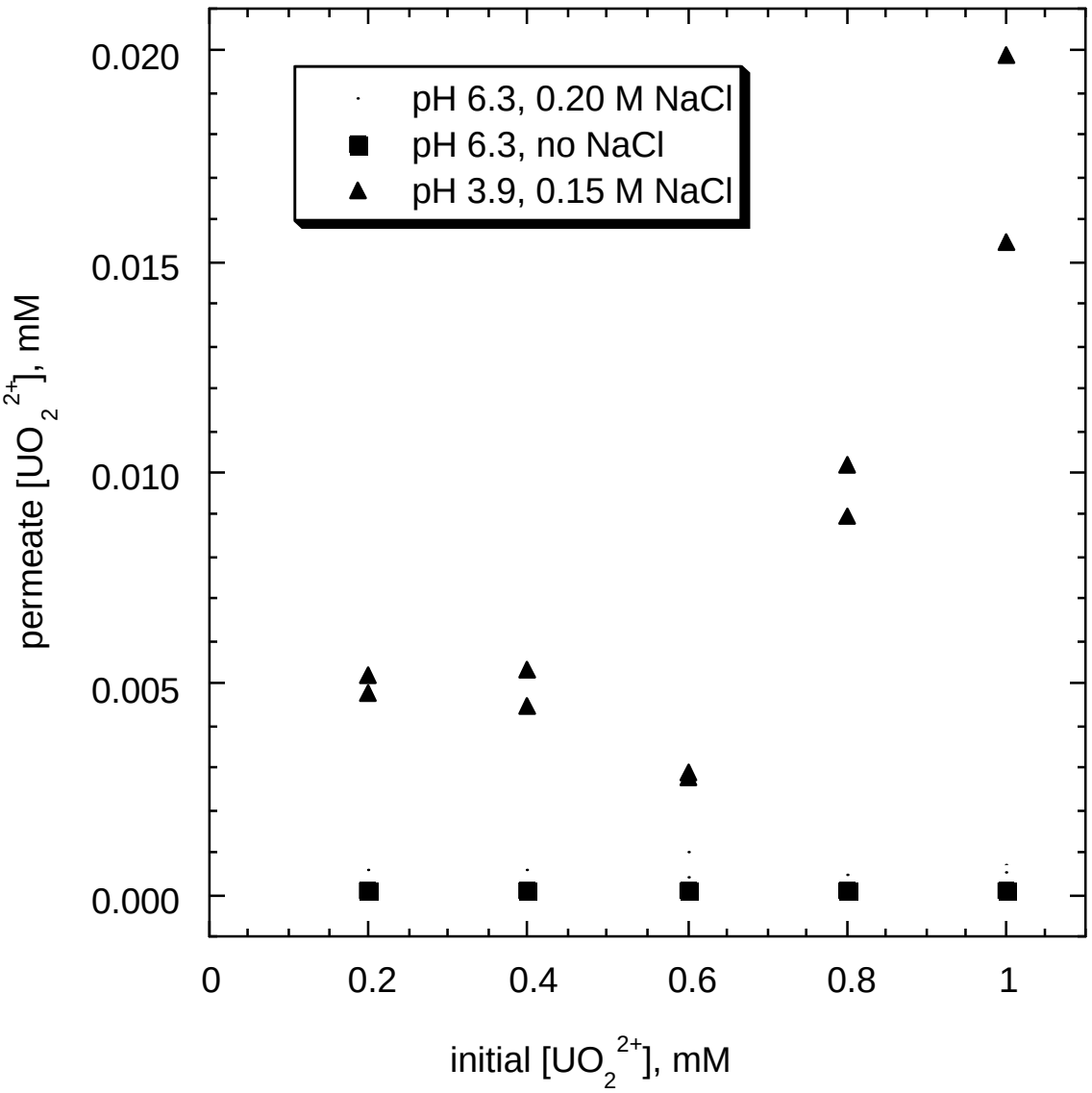
Preliminary studies using 4,5-dihydroxybenzene-3,5-disulfonic acid as a ligand for UO_2^{2+} were carried out using ED and UF. In particular, the ED studies investigated the effects of pH (~6.3, 3.9) and added electrolyte (0.0, 0.2 M NaCl) on separation performance for UO_2^{2+} concentrations in the range 0.19 - 0.96 mM. UF studies at pH ~5 and $[DHBDSA]_0 = [UO_2^{2+}]_0 = 0.25$ mM were carried out in the absence and presence of added electrolyte (0.2 M NaCl). The results of these studies are shown in the following two panels.

In the ED studies at pH 6.3 without added salt, $R_{UO2} \geq$ **99.95%** for all UO_2^{2+} concentrations employed. The range of rejection values decreases slightly, R_{UO2} = **99.74% - 99.94%**, in the presence of 0.2 M NaCl. When the pH is lowered to 3.9 the rejection decreases further, but is still appreciable; R_{UO2} = **96.77% - 99.34%** .

Similar performance was observed in the UF studies with average UO_2^{2+} rejections of **99.91%** and **99.82%**, in the absence and presence of NaCl, respectively.

Equilibrium dialysis results for UO_2^{2+} with DHBDSA: Effects of pH, $[NaCl]_0$, and $[UO_2^{2+}]_0$

$[DHBDSA]_0$ = 1.0 mM, [PDADMAC] = 20.0 mM



Ultrafiltration results for UO_2^{2+} - DHBDSA - PDADMAC

$[UO_2^{2+}]_0$ = 0.26 mM, $[DHBDSA]_0$ = 0.26 mM, PDADMAC = 5.0 mM, pH 5.0, average sample vol. = 26.5 mL, flow rate = 2.5 mL / min.

NaCl = 0.0

Sample #	$[UO_2^{2+}]_{per}$, mM	$[UO_2^{2+}]_{ret}$, mM	R_{UO2} (%)
1	0.0007	0.289	99.76
2	0.0003	0.346	99.91
3	0.0002	0.425	99.96
4	0.0004	0.535	99.93
5	0.0003	0.662	99.95
6	0.0002	0.859	99.98
		Ave. R_{UO2} (%) =	**99.91**
ED result using same initial solution:		R_{UO2} (%) =	99.88

NaCl = 0.2 M

Sample #	$[UO_2^{2+}]_{per}$, mM	$[UO_2^{2+}]_{ret}$, mM	R_{UO2} (%)
1	0.0009	0.307	99.71
2	0.0008	0.355	99.77
3	0.0008	0.418	99.81
4	0.0006	0.509	99.88
5	0.0007	0.652	99.89
6	0.0008	0.858	99.91
		Ave. R_{UO2} (%) =	**99.83**
ED result using same initial solution:		R_{UO2} (%) =	99.68

SUMMARY: Both ligands provide excellent rejection of UO_2^{2+} using ED and UF methods.

Carbonate ($NaHCO_3$ / Na_2CO_3)

<u>Equilibrium Dialysis</u> for [UO_2^{2+}] in the 0.1 - 1.0 mM range;

Rejection values ≥ 99.9% at pH 7.8

Rejection values ≥ 99.4% at pH 10.5

0.2 M NaCl causes a decrease in R_{UO2} to ~30-40%%

At pH 2.3, there is expulsion of UO_2^{2+} into the permeate.

<u>Ultrafiltration</u> for [UO_2^{2+}] = 0.25 mM;

Rejection values ≥ 99.6% for pH 6.8 -10.5;

0.5 M NaCl causes a decrease in R_{UO2} to ~ 82.0%

At pH 2.6 rejection of UO_2^{2+} decreases to 74.7%.

DHBDSA (4,5-dihydroxy-1,3-benzenedisulfonic acid)

<u>Equilibrium Dialysis</u> for [UO_2^{2+}] in the 0.2 - 1.0 mM range;

Rejection values ≥ 99.9% at pH 6.3 (no NaCl)

Rejection values ≥ 99.7% at pH 6.3 (0.2 M NaCl)

Lowering pH to ~3.9 gives R_{UO2} = 96.8-99.3% (0.15 M NaCl).

<u>Ultrafiltration</u> for [UO_2^{2+}] = 0.26 mM; pH 5.0 ;

Rejection values ≥ 99.9% (no NaCl); ≥ 99.8% (0.2 M NaCl)

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