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Beryllium Binding by Functionalized Polyethylenimine Water-Soluble Polymers

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ABSTRACT

A series of polyethylenimine (PEI)-based water-soluble polymers (WSPs) were prepared by attaching functional groups (beta-diketones, carboxylic acid, salicylic acids) to the polymer backbone, with the goal of characterizing the interaction between beryllium and the various polymers. The extraction of beryllium from aqueous solutions by the WSPs was examined as a function of pH and ionic strength to evaluate the potential for the WSPs to isolate beryllium from contaminated aqueous waste streams. The loading capacities of these polymers for beryllium at near-neutral pH were unusually high in the absence of ionic strength adjustment compared to that for other $+2$ cations, suggesting that polynuclear beryllium species were interacting with the polymers. Beryllium loading capacity values were similar for all polymers evaluated in the absence of ionic strength adjustment. However, when the ionic

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strength of the solutions was adjusted to 0.1 N ($NaNO_3$) the loading capacities were significantly reduced, indicating that electrostatic attraction played a dominant role in the interaction between beryllium and the polymers. The extraction curves of beryllium for all polymers evaluated, even those not designed to be selective for beryllium extraction, were nearly identical irrespective of the nature of the functional groups. Collectively, these results suggest that oligomeric beryllium species were formed, which can bind to the polymers through a combination of electrostatic forces and, potentially, hydrogen bonding.

Key Words: Beryllium; Water-soluble polymers; WSP; Polyethylenimine; PEI.

INTRODUCTION

Beryllium is a strategic metal because of its extraordinary materials properties; it is lighter than aluminum and six times stiffer than steel. Often alloyed with other metals such as copper, beryllium is a key component in the aerospace, electronics, and nuclear industries. As with many industrially important metals, the use of beryllium in these enterprises has lead to environmental contamination and the need for remedial action. Environmental contamination is of particular concern because human exposure to beryllium through inhalation can result in the development of Chronic Beryllium Disease (CBD), a serious, often fatal lung disease.[1] Ironically, it is the hazards associated with handling beryllium that have limited fundamental studies on speciation and environmental extraction. Very limited information on the coordination chemistry of beryllium and the extension of this chemistry to practical environmental cleanup is available.

Not surprisingly, the separation of beryllium from the environment is a complex and challenging problem. Beryllium forms extremely stable oxides that are difficult to extract because of the low kinetic lability exhibited by beryllium when ligated by oxygen donors.[2,3] As a consequence of its small size and high charge, the beryllium cation has an extremely small ionic radius and a propensity to form strong covalent bonds with ligands containing hard donors like oxygen and nitrogen. In general, the aqueous chemistry of beryllium is dominated by its hydrolysis chemistry. While there is debate concerning the exact identification of species present in aqueous solution, it is clear that in the absence of competing ligands, the aquo cation $[Be(H_2O)_4]^{2+}$ is readily hydrolyzed between pH 3 and 6 to give polynuclear species such as $[Be_3(OH)_3]^{3+}$, $[Be_2(OH)]^{3+}$, and $[Be_6(OH)_8]^{4+}$.[4–10] The identification of

$[Be_3(OH)_3]^{3+}$ as the dominant polynuclear species in this pH range has been confirmed by single-crystal X-ray structure analysis of compounds such as $Be_3(OH)_3$(picolinate)$_3$ and $Be_3(OH)_3$(pyrazolylborate)$_3$[11] and through ^{9}Be NMR.[4,9] In the absence of complexing or solubilizing ligands extensive hydrolysis of beryllium leads to the formation of insoluble $Be(OH)_2$ from pH 6 to 8. At higher pHs, amphoteric beryllium forms soluble polynuclear beryllates such as the trimer $[Be(OH)(H_2O_2)]_3^{3+}$ or $Be_4(OH)_{10}^{2-}$.[4,10,11]

Suitable ligands for beryllium binding usually have small bite sizes and are able to form 6-membered chelate rings. To date, most of the studies on beryllium coordination or extraction chemistry have focused on complexation of beryllium by simple carboxylic acids such as salicylate, oxylate and malonate, beta diketones, salicylic acids, and catechols.[12–16] Nitrilotripropionic acid, nitrilo(2-ethylenepyridine bis(3-propionic) acid, and nitrilotris-(ethylenephosphonic) acid have also been suggested as possible sequestering agents for beryllium.[3] Beryllium complexes usually form polynuclear aggregates, as can be seen in $Be_4O(O_2CR)_6$,[17–21] $Be_6O_2(O_2CMe)_8$,[22] $Na_4[Be_6(OCH_2CO_2)_8]$,[23] and $K_3[Be_3(OH)_3$(malonate)$_3 \cdot 6H_2O$.[5] These observations are consistent with the existence of various hydrolytic polynuclear species of beryllium in aqueous solution.

Interest in beryllium coordination chemistry and environmental speciation stems from the need to selectively remove and mobilize beryllium from contaminated soils and debris that exists at Department of Energy sites and beryllium industrial manufacturing and machining facilities. Water-soluble chelating polymers have proven effective in removing metal ions from aqueous systems such as industrial wastes, nuclear wastes, and natural waters as well as soils.[24–27] One of the most significant features of WSPs as extractants is the ease with which many commercially available polymer backbones can be modified with specific chelators to achieve the desired selectivity for a specific metal ion or for a class of contaminants.[28] Guided by the immense database on thermodynamic properties of chelators, polymers with a wide range of selectivity can be prepared by the covalent attachment (functionalization) of potentially appropriate chelators.[24,29–33] Researchers at Los Alamos National Laboratory (LANL) have used commercially available polyethylenimine (PEI) and functionalized derivatives for the recovery and separation of actinides for analytical, environmental, and processing applications[25,34,35] as well as for the extraction of lead from contaminated soils and debris.[26,27] PEI, a highly soluble branched polyamine (Fig. 1) can be readily modified by reacting primary and secondary amines with ligands to enhance metal binding.[25] Polymers can be readily recovered using ultrafiltration.[26,33]

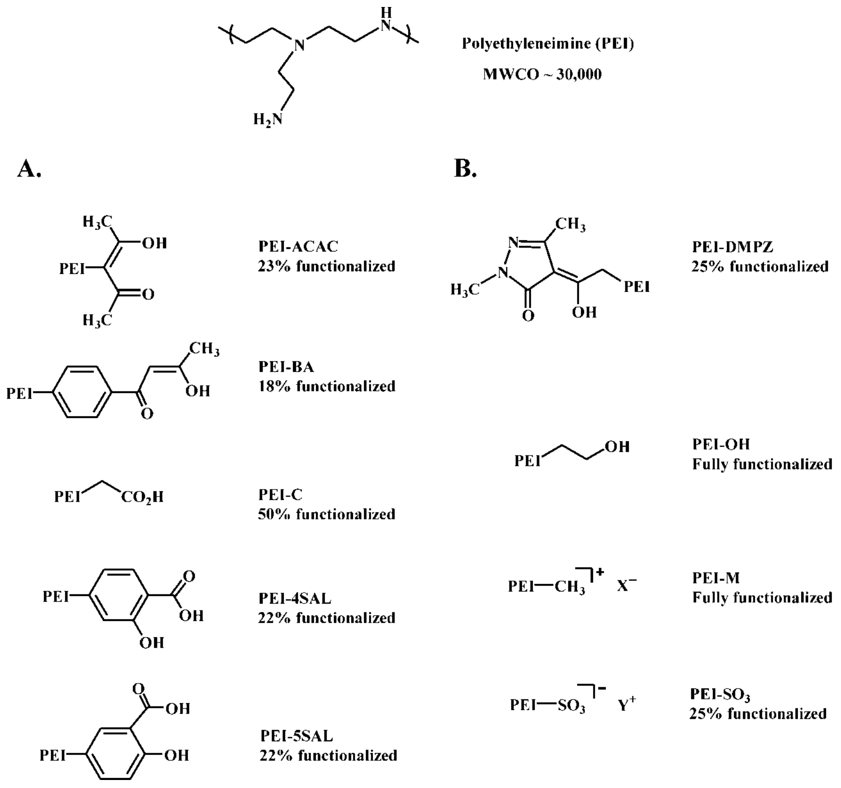

Figure 1. Water-soluble polymers evaluated for beryllium extractions.

The objective of research conducted in this study was to characterize interactions between beryllium and WSPs with different functionalities. Given the success with which this approach has been applied to other metal ions, it was anticipated that WSPs could be designed to selectively extract beryllium from aqueous media. PEI-based polymers were prepared by attaching functional groups, including acetylacetone, benzoylacetone, carboxylic acid, and salicylic acids, to the polymer backbone. Literature data suggest that these ligands have high affinity for beryllium. Representative stability constant values are documented in Table 1. It was anticipated that the polymer-bound ligands would have similar affinity for beryllium. Additionally, several polymers were prepared that were not predicted to have a propensity to interact with beryllium for comparison with previous polymers. For example, hydroxyl functionalized PEI-OH is neutral and cannot

Table 1. Stability constants of beryllium complexes.

Ligand	Log K_1 (ML/M.L)	Log K_2 ($ML_2/M.L_2$)	Temp (°C), ionic strength
Acetylacetone	7.49	14.38	25, 0.1
Salicylic acid	12.37	22.02	20, 0.1
Catechol	13.52	23.35	20, 0.1

Martell, E. A, Smith, M. R; Critical stability constants, V. 1, 3 and 6; Plenum Press, NY.

coordinate beryllium. Finally, two polymers with sites of permanent cationic or anionic charge and limited complexing ability were prepared, permethylated polyethylenimine (PEI-M) and PEI functionalized with ethanesulfonic acid (PEI-SO_3), respectively, to explore the significance of electrostatic interactions on beryllium binding.

EXPERIMENTAL

Chemicals and Reagents

Branched PEI was obtained from BASF Corp. (Mount Olive, NJ, USA) and purified by diafiltration using a hollow-fiber polysulfone membrane cartridge of molecular weight cutoff (MWCO) less than 30,000 provided by A/G Technology Corp. (Needham, MA, USA). Solutions were concentrated by rotary evaporation and vacuum dried at 63°C prior to functionalization. 3-Chloro-2,4 pentadione, 4-chlorosalicylic acid, 5-chlorosalicylic acid, triethylamine, and all other chemicals and solvents for polymer synthesis and characterization were purchased from Aldrich (Milwaukee, WI, USA) or Acros (Metuchen, NJ, USA) in analytical grade and used without further purification. Standard solutions of metal ions were purchased from SPEX (Acros). Sodium nitrate ($NaNO_3$), potassium hydroxide (KOH), and hydrochloric acid (HCl) were obtained from J.T. Baker, Inc. (Baker Analyzed, Phillipsburg, NJ, USA). Water was purified using a Milli-Q® system for all experiments.

Membrane Separations

Diafiltration of polymers was performed using a Quixstand® bench-top hollow-fiber membrane system (30,000 MWCO) from A/G Technology

Corp. Ultrafiltration of polymers was performed using Amicon® filtration units (Centricon®-10, Centriplus®-10, or Centriprep®-10, 10,000 MWCO, Millipore Corp, Bedford, MA, USA). The aqueous solution was placed in the retentate portion of the unit and was centrifuged until approximately half of the volume was filtered through the membrane. Species greater than 10,000 MW units (e.g., complexes of metal ions and polymer, uncomplexed polymer, beryllium oligomeric clusters) were retained in the retentate chamber while the small species (e.g., unbound metal ions, electrolytes) passed through the membrane.

Analytical

Metal ion concentrations were measured by a Varian Liberty 220 inductively coupled plasma atomic emission spectrometer (ICP-AES). An Orion Research 611 pH meter equipped with a glass combination pH electrode was used for pH measurements. Proton NMR spectra were recorded with a Varian Unity Inova 300, using tetramethylsilane as the reference. Infrared (IR) data were recorded with a Nicolet Avatar 360-FTIR. Elemental analyses were performed using a Perkin–Elmer PE 2400, (Series II) Elemental Analyzer.

Synthesis of Functionalized Water-Soluble Polymers (WSPs)

The following polymers were prepared according to the literature[25]: PEI-C (PEI functionalized with chloroacetic acid), PEI-DMPZ (PEI functionalized with dimethylpyrazolone), PEI-M (permethylated PEI). The polymer PEI-OH was prepared by the reaction of purified PEI with bromoethanol.[36] The remaining polymers were prepared according to synthesis procedures described in the proceeding paragraphs. The degree of functionalization is expressed as a percentage of the primary and secondary amines that can be functionalized.

PEI-ACAC (PEI functionalized with acetylacetonate): An aqueous solution (20 mL) of 3-chloro-2,4 pentadione (3.15 g, 23.37 mmol) in triethylamine (4.73 g, 46.75 mmol) was added dropwise into a warm, stirred aqueous solution (100 mL) of PEI (4.03 g, 93.50 mmol) over 20 minutes. The solution was then heated and refluxed for 5 hours, during which time the solution color changed from yellow to reddish brown. The mixture was cooled to room temperature overnight and then purified by diafiltration using a 30,000 MWCO polysulfone membrane and 8 L of deionized water. After diafiltration, the solution volume was reduced by rotary evaporation. The resulting solid was dried under vacuum at 60°C. This yielded 3.97 g of a red brown solid (64.7%). [IR(cm − 1): 1650 (C=O), 3430 (N—H); ^{1}H NMR(H_2O,ppm): 1.781(s), 4.79–4.58 (b, PEI); EA: C: 53.45%; H: 9.31%; N:19.49%; calculated degree of functionalization: 23%]

PEI-BA (PEI functionalized with benzoylacetone): PEI-BA was synthesized and purified similarly to PEI-ACAC, using PEI (4.00 g, 93.49 mmol), 1-bromobenzoylacetone (4.88 g, 23.33 mmol), and triethylamine (4.70 g, 46.73 mmol). After refluxing 30 hours, 2.65 g of product was isolated after preparation as a yellow solid, yield 39.6%. [IR(cm − 1): 1690 (C=O), 3455 (N—H); ^{1}H NMR(H_2O,ppm): 7.4–7.8(m,b), 1.92(s), 4.72–4.59 (b, PEI); EA: C: 45.03%; H: 9.30%; N: 20.93%; calculated degree of functionalization: 18%]

PEI-SO_3 (PEI functionalized with ethanesulfonic acid): A solution of NaOH (6.5 g, 163 mmol) was added to 50 mL aqueous solution of 7.0 g (163 mmol) of PEI and cooled to 5°C. After 1 hour, 350 mL of an aqueous solution of 85.7 g (406 mmol) 2-bromoethanesulfonic acid was added dropwise over 45 minutes at 5°C. The mixture was then refluxed for 3 hours, cooled, and allowed to stir overnight. Saturated KOH was added until the pH reached 12.5. After stirring, HCl was added to bring the pH to 10. The product was purified by diafiltration, rotary evaporated to near dryness, and then dried under vacuum to give a dark yellow solid at a yield of 8.16 g, (66.2%). [IR(cm − 1): 1654 (C=O), 3447 (N—H). EA: C: 37.1%; H: 8.35%; N: 16.97%; calculated degree of functionalization: 25%]

PEI-5SAL (PEI functionalized with 5-chlorosalicylic acid): A solution of 2.00 g (11.61 mmol) of 5-chlorosalicylic acid was dissolved in a warm aqueous solution (25 mL) of 3.81 g (34.83 mmol) triethylamine. The mixture was added dropwise to an aqueous solution (100 mL) of 2 g (46.44 mmol) of PEI. The whole solution was refluxed for 48 hours, during which time its color changed from pale to bright yellow. The product was purified by diafiltration and lyophilized to give 2.91 g of a bright yellow solid (85.5%). [IR(cm − 1): 1585 (C=O), 3460 (N—H); 1H NMR (H_2O,ppm): 7.53(s), 7.0(d), 6.62(d) 4.78–4.65 (b, PEI); EA: C 47.05%; H 6.98%; N 14.61%; calculated degree of functionalization: 22%]

PEI-4SAL (PEI functionalized with 4-chlorosalicylic acid): This polymer was prepared in the same manner as PEI-5SAL using PEI (2.00 g, 46.44 mmol), 4-chlorosalicylic acid (2.00 g, 11.61 mmol), and triethylamine (2.54 g, 23.23 mmol). The product had a slightly brown color with a yield of 2.80 g (82.4%). [IR(cm − 1): 1590 (C=O); 1H NMR(H_2O,ppm): 7.6(d), 6.74(s), 6.70(d) 4.78–4.65 (b, PEI); EA: C 47.87%; H 7.06%; N 13.87%; calculated degree of functionalization: 22%]

Metal Binding Studies

Loading capacity studies were performed at a single pH value to determine the concentration of beryllium that could be bound to representative polymers (PEI, PEI-C, PEI-ACAC, PEI-5SAL). Loading capacity studies were performed with and without ionic strength adjustment (0 vs. 0.1 M $NaNO_3$) at a beryllium:polymer ratio of 1:2 (all metal:polymer ratios are expressed as weight:weight). Beryllium extraction curves were produced as a function of pH at a beryllium:polymer ratio of 1:40 in the presence of 0.1 N $NaNO_3$. Beryllium concentrations in all experiments ranged from $20\,mg\,L^{-1}$ to $100\,mg\,L^{-1}$. The pH was adjusted by addition of either HCl or KOH. Beryllium-containing solutions were contacted with polymers for 14 days on a rotating shaker (LabQuake®) to ensure equilibrium conditions were achieved. After the extraction was complete, solutions were filtered through a 10,000 MWCO ultrafiltration membrane. To determine whether loss of metal ions had occurred due to metal ion hydrolysis, a mass balance of metals before and after contact with polymers was measured for each extraction experiment. The volumes of the retentate and permeate were monitored, and the metal ion concentrations of the retentate and permeate were measured by ICP-AES.

Experiments were also performed to evaluate the retention of beryllium oligomers by ultrafiltration through 10,000 MWCO membranes as a function of pH in aqueous solutions of pure water and 0.1 N $NaNO_3$ solutions. Batch samples were prepared in 15-mL centrifuge tubes using MilliQ water, $20\,mg\,L^{-1}$ beryllium, and 0.1 N $NaNO_3$ prepared in MilliQ water within the pH range of 3 to 10. Solutions were rotated for 2 days at 22°C. Samples were centrifuged at 2500 rpm for 1 hour. A portion of the aqueous phase samples was then ultrafiltered through a 10,000 MWCO Centricon filter at 2500 rpm for 30 minutes. Unfiltered, centrifuged samples and ultrafiltered samples were then analyzed by ICP-AES.

RESULTS AND DISCUSSION

With the goal of designing and synthesizing soluble polymers for selective complexation of beryllium from aqueous systems, polymers containing beta-diketone, carboxylic acid, and salicylic acids ligands were prepared by metathesis reactions with PEI. Figure 1A shows the structure of the attached ligands and the degree of PEI functionalization based on elemental analysis for PEI-ACAC, PEI-BA, PEI-C, PEI-4SAL, and PEI-5SAL. Typical functionalization levels for these polymers were approximately 20%. Attempts to prepare materials with higher concentrations of ligand led to polymers with lower solubility. PEI-C is the exception, being soluble even when 100% of the primary and secondary amines were functionalized. Additionally, PEI-DMPZ, PEI-OH, PEI-M, and PEI-SO_3 (Fig. 1B) were prepared to evaluate the interactions of these polymers with beryllium for comparison with polymers designed to be selective for beryllium (Fig. 1A).

Loading Capacity Studies

Beryllium loading capacities for PEI-ACAC, PEI-C, and PEI-5SAL, polymers prepared for selective binding of beryllium, were performed using a beryllium:WSP ratio of 1:2. For comparison, the loading capacity of PEI was also evaluated. All capacities were measured with and without 0.1 N $NaNO_3$. Table 2 provides a comparison of the capacities of the representative polymers for beryllium. In the absence of ionic strength adjustment the beryllium capacities are all high and on the same order of magnitude. For example, PEI-ACAC bound 28.41 mmol of beryllium per g of polymer. This capacity corresponds to approximately 1.5 beryllium atoms per nitrogen donor or 6–7 beryllium atoms per ACAC ligand on the polymer. This result indicates that the PEI functionalized polymers were not binding individual beryllium ions but rather were stabilizing polynuclear hydrolysis products of beryllium near pH 6.0. It is interesting to note that the unfunctionalized PEI, with only nitrogen donors, also bound high levels of beryllium. The capacities were significantly reduced when measured in the presence of a 0.1 N $NaNO_3$ ionic strength buffer.

Table 2. Loading capacity of WSPs for beryllium.

WSP	pH	Ionic strength (N)	LC (mmol/g P)
PEI	5.97 (+/− 0.25)	0	29.38 (+/− 1.44)
PEI	5.95 (+/− 0.05)	0.1	3.60 (+/− 2.29)
PEI-ACAC	5.98 (+/− 0.21)	0	28.41 (+/− 0.11)
PEI-ACAC	5.95 (+/− 0.05)	0.1	3.13 (+/− 3.40)
PEI-C	5.94 (+/− 0.25)	0	19.87 (+/− 4.73)
PEI-C	5.95 (+/− 0.05)	0.1	2.80 (+/− 1.22)
PEI-5SAL	6.08 (+/− 0.08)	0	23.97 (+/− 5.32)
PEI-5SAL	5.95 (+/− 0.05)	0.1	1.07 (+/− 0.21)

Loading capacity experiments were performed in the absence of ionic strength adjustment with several other $+2$ metal cations of environmental significance (Ca^{2+}, Mg^{2+}, Cu^{2+}, Pb^{2+}, and UO_2^{2+}) to compare the capacities of the polymers for other metals with that of beryllium. Table 3 shows representative loading capacities (mmol metal per g of polymer) of PEI, PEI-C, and PEI-ACAC for lead, copper, and uranium in the absence of ionic strength adjustment. The three polymers had modest affinity for the metals with capacities similar to those observed for other metals on polyamine polymers. The polymers had no affinity for the common impurity metals calcium and magnesium. These results suggest that beryllium is forming oligomeric species at near pH 6 that are electrostatically stabilized by the PEI functionalized polymers in the absence of ionic strength adjustment, or that beryllium oligomeric species formed are large enough to be separated from permeate during ultrafiltration and therefore may not be entirely bound to the polymers. In contrast to other metal ions, there are only a few reports investigating beryllium colloids.[37] The pore size range of 10,000 MW cutoff membranes is 5×10^{-9} to 10^{-8} m. Colloidal systems are characterized by particles ranging in size from 10^{-9} to 10^{-6} m; therefore, if beryllium colloids in the larger size range formed, they could be retained along with the polymer by the membranes used in this study. To verify whether beryllium oligomeric species were retained in the retentate chamber of the ultrafiltration centrifuge tubes, experiments were performed near pH 6 in the absence of polymer with and without ionic strength adjustment (0.1 N $NaNO_3$).

To evaluate beryllium retention by ultrafiltration devices as a function of pH in aqueous solutions of pure water and 0.1 N $NaNO_3$ solutions, batch samples were prepared in similar fashion to previous experiments with the omission of polymers. Fig. 2 a) and b) summarize the experimental results. Beryllium began to hydrolyze and precipitate above pH 5.7. Ionic strength did not have a significant impact on the pH at which precipitation was first observed. At and above pH 6.0 the difference between beryllium concentrations in the centrifuged-only versus ultrafiltered samples increased in dramatic fashion, especially for samples without ionic strength adjustment. For example, at pH 6.08 without ionic strength adjustment, 64% of the beryllium in solution was retained by the ultrafilter, whereas for the 0.1 N sample at pH 6.10 only 18% of the beryllium was retained by the ultrafilter. At pH 6.3, 88% of aqueous phase beryllium was retained by the filter without ionic strength adjustment, whereas 54% of the beryllium was retained for the 0.1 N sample at 6.41. The 10,000 MWCO ultrafilters retained aqueous-phase beryllium above pH 6.0. If colloidal species of beryllium formed below pH 6.0, they were of a small enough size to move through ultrafiltration

Table 3. Loading capacities of WSPs for various metal ions.

	PEI		PEI-C		PEI-ACAC	
Metal ion	pH	LC (mmol/g P)	pH	LC (mmol/g P)	pH	LC (mmol/g P)
Cu	6.74 (+/− 0.25)	4.72 (+/− 0.20)	Not available	Not available	6.74	6.80
Pb	6.34 (+/− 0.25)	1.45 (+/− 0.22)	6.75 (+/− 0.11)	1.69 (+/− 0.27)	5.60	0.35
UO_2	6.75 (+/− 0.25)	4.72 (+/− 0.40)	6.75 (+/− 0.32)	0.59 (+/− 0.20)	7.09 (+/− 0.04)	0.92 (+/− 0.08)

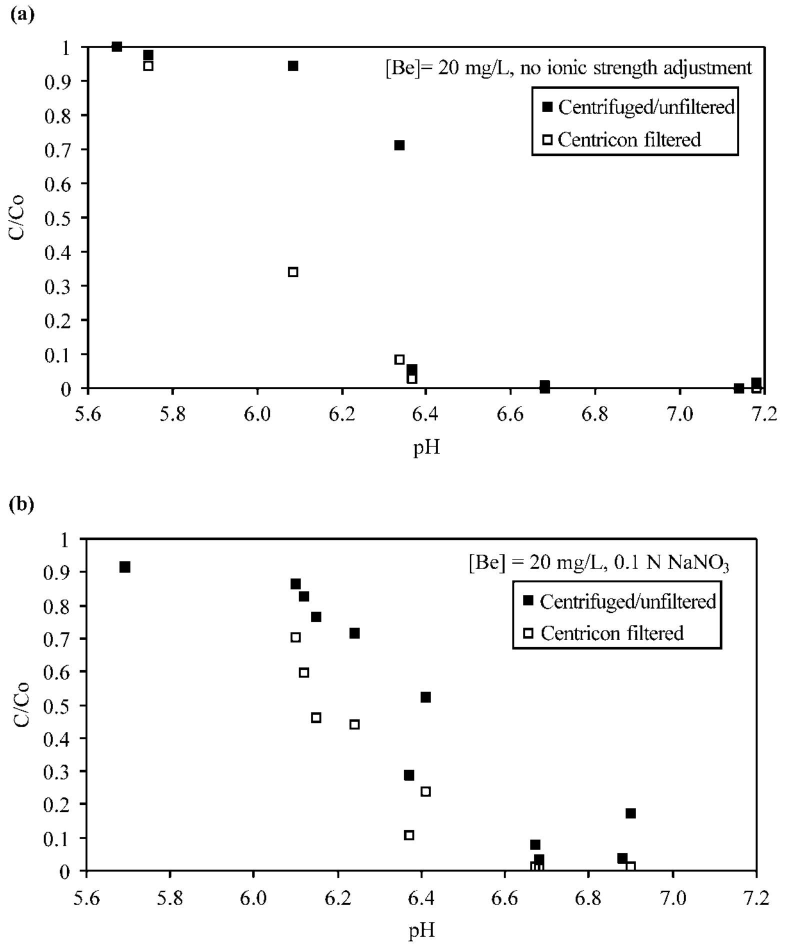

Figure 2. Concentration of beryllium [$C_{o,Be} = 20\,mg\,L^{-1}$] remaining in solution as a function of pH and ultrafiltration for a) no ionic strength adjustment and b) 0.1 N $NaNO_3$.

membranes. Above pH 7.0 all beryllium had precipitated from samples with and without ionic strength adjustment.

These studies showed that without WSP, even dilute solutions of beryllium (20 ppm) hydrolyzed and formed precipitates of $Be(OH)_2$ at pHs ≥ 5.7. Precipitation was not observed at near pH 6.0 for any of the polymer loading capacity experiments; therefore the polymers were certainly interacting with beryllium. In the presence of WSPs, hydrolysis of beryllium was either suppressed, or more likely, the hydrolyzed species were stabilized in solution by the polymer systems through electrostatic or hydrogen-bonding interactions. It has been reported that beryllium forms pseudocolloids (surface-sorbed colloidal species) at $\mathrm{pH} > 4$ and that they are most abundant from pH 8 to 11.[37] However, in experiments without polymers no evidence for retention of beryllium in solutions separated by ultrafiltration was observed when the pH was less than 5.7. Beryllium retentate and permeate concentrations were identical by ICP-AES analysis of samples until the pH reached approximately 5.7 and precipitation occurred. Colloidal species large enough to be retained during ultrafiltration were not formed by our systems prior to the observation of $\mathrm{Be(OH)_2}$ precipitation. The beryllium aqueous solution batch experiments provided evidence that beryllium in solution within the pH range 6.0 to 7.0 was retained by 10,000 MWCO filters due to the size of beryllium oligomers. It is also important to note that the differences in percentages of beryllium retained by the ultrafiltration membranes for the samples with no ionic strength adjustment versus 0.1 N ionic strength were not great enough to account for the large variation between loading capacity values observed in Table 2. To further explore the interaction between the various polymers and beryllium, retention experiments were performed as a function of pH. These experiments were conducted using 0.1 N $\mathrm{NaNO_3}$ ionic strength to minimize the impact of beryllium oligomer formation.

Beryllium Retention Curves

Beryllium retention by 10,000 MWCO membranes was evaluated as a function of pH from 1 to 10 for the functionalized PEI polymers. Representative retention curves for PEI-BA, PEI-C, PEI-DMPZ, PEI, and PEI-OH are shown in Fig. 3, and those for PEI-5SAL and PEI-4SAL are shown in Fig. 4. Several significant features are apparent. Of the nine polymers evaluated in this study, only PEI-C was able to stabilize beryllium and prevent precipitation of $\mathrm{Be(OH)_2}$ above pH 7. In the absence of the polymers, beryllium precipitation started at approximately pH 5.7. For all polymers, beryllium retention occurred over a very narrow pH range, from approximately pH 5.6 to 7.0, and the binding curves were virtually identical. The only notable deviation from this behavior was that PEI-5SAL and PEI-4SAL exhibited higher retention of beryllium than did the other polymers between pH 4 and 6 (Fig. 4). This retention is most likely due to complexation of the beryllium to the salicylic acid between pH 4 and 6. The similarity

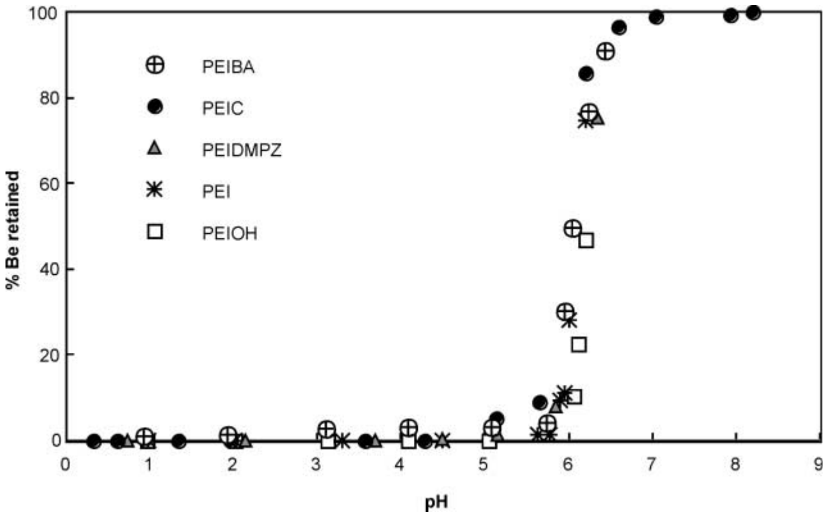

Figure 3. Representative retention curves for beryllium, [$C_{o,Be} = 20\,mg\,L^{-1}$, WSPs $= 800\,mg\,L^{-1}$, 0.1 N $NaNO_3$).

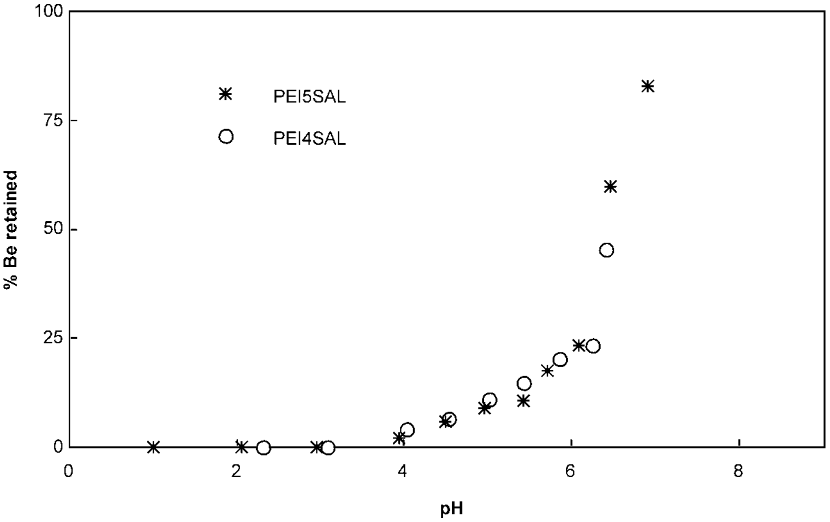

Figure 4. Extraction curves of PEI-4SAL and PEI-5SAL for beryllium.

between the beryllium extraction curves with these polymers is atypical and is not seen for other metals. Given the variation in the dissociation constants (pKa) for these ligands [SAL = 22[29]; ACAC = 8.80[29]; BA = 8.89[29]; aminoacetic acid = 9.57[30]; DMPZ = 4.73[38]], beryllium binding to the polymers should have exhibited different pH profile retention behavior if beryllium coordination was an important component in the beryllium–polymer interaction. For example, the beryllium binding curve for DMPZ should be shifted to significantly lower pH if beryllium was coordinated to the ligand.

These results are consistent with the conclusion that the attached ligands did not impact beryllium interaction with the PEI-based polymers in the pH range 5.6 to 7.0. Conventional chelation to the ligands was not occurring in these systems. A number of other observations also support this conclusion and suggest that electrostatic and hydrogen bonding were the dominant interactions between beryllium and the polymers. For example, variations in the degree of polymer functionalization did not affect beryllium binding. The ACAC and DMPZ polymers were functionalized at approximately 20% and PEI-C at 50%. The higher functionalized polymers displayed the same binding capacities and pH behavior with beryllium as did lower functionalized polymers and the unfunctionalized polymer, PEI.

The direct coordination of beryllium to unfunctionalized amine nitrogens alone is unlikely, given the low affinity of beryllium for amines, the high positive charge on the polymer backbone at near neutral pH, and the observation that beryllium capacities did not alter dramatically with the level of polymer functionalization. Additionally, fully functionalized PEI-OH, which cannot coordinate beryllium and is uncharged at neutral pH, had an extraction curve that was identical to the other polymers at pH values less than 6.2; however, above pH 6.2, PEI-OH did not have the ability to keep beryllium from precipitating (Fig. 3). These results suggest that a combination of hydrogen bonding and electrostatic interactions controlled the binding of beryllium to the polymers.

The hydrolysis of beryllium leads to the formation of cationic beryllium clusters such as $[Be_3(OH)_3]^{3+}$ and $[Be_6(OH)_8]^{4+}$ above pH 5.[39] Hydrogen bonding between the beryllium hydroxo clusters and amine and ligand-functionalized polymers may stabilize the hydrolyzed species and prevent precipitation of $Be(OH)_2$. Electrostatic interactions between these species and the polymers are also possible depending on the attached functional group. The potential for electrostatic binding of hydrolyzed beryllium species to several PEI-based polymers was examined through a series of additional experiments.

The binding of beryllium to polymers with permanent cationic and anionic functionality (PEI-M and PEI-SO_3, respectively) exhibited the same interaction as the other polymers examined. Specifically, there was no binding except at near-neutral pH, and precipitation occurred above pH 6.2. Given these results, we conclude that electrostatic interactions cannot be solely responsible for beryllium interactions with the soluble polymers and that hydrogen bonding is also important in stabilizing beryllium in solution at pH values greater than 5.7.

The nearly identical beryllium binding curves for all polymers and the effect of ionic strength on beryllium binding to the polymers confirm that beryllium was not complexed to these polymer systems or bound predominantly through ionic interactions. We suggest that as a consequence of its high charge-to-size ratio and its strong hydrolytic character, beryllium clusters or oligomers, which form as solution pH is increased above pH 5.7, are prevented from aggregating and are thus solubilized through hydrogen bonding to the hydrogen donor sites on the polymers as well as through electrostatic interactions.

CONCLUSIONS

A number of PEI-based WSPs were synthesized and their binding capacities with beryllium and other metal ions were investigated. Studies of the binding of beryllium to these polymeric extractants show that interaction of the beryllium with the polymers occurred within a very narrow pH range, 5.6–7.0, with the exception of PEI-C, which may actually be stabilizing the beryllium due to classic complexation. As with the other metal-binding polymers it was anticipated that the polymers would coordinate single beryllium atoms at the attached ligand sites. However, this was not seen. A series of experiments were undertaken to assess the nature of the interaction of beryllium with the WSPs. These studies showed that beryllium binding was not dramatically affected by polymer functional group; however, ionic strength had a significant impact on loading capacities. Formation and retention of beryllium colloidal species were also evaluated through a series of control experiments. We suggest that as a consequence of its high charge-to-size ratio and its strong hydrolytic character, beryllium clusters or oligomers, which form as solution pH is increased above pH 5.7, were prevented from aggregating and thus solubilized through hydrogen bonding to the hydrogen donor sites on the polymers. This unusual binding mode manifests itself in several ways. First, the capacities of the polymers for beryllium (mmoles of beryllium bound/g polymer) are much higher when compared with those for other metal ions. Second, we observed that regardless of the ligand attached to the polyamine support, the pH profiles for beryllium binding were identical. No variation in beryllium binding occurred despite significant differences in the pKa's for the ligands. Finally, the binding of the beryllium in these systems is highly pH dependent; beryllium binding in these systems occurs only above pH 5.6. In particular, the strong dependence of beryllium binding on pH supports the assertion that beryllium speciation plays a critical role in the interactions of this metal with hydrogen-bonding polymer systems. The beryllium-polymer interaction occurs at the pH where models predict that beryllium speciation changes from $Be(H_2O)_6^{2+}$ to $[Be_3(OH)_3]_3^{3+}$. We believe that the stabilization of beryllium-hydroxo species through hydrogen bonding is favored over classic coordination in these multidentate polymers.

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