

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Selective Anion Binding from Water Using Soluble Polymers

Eva R. Birnbaum^a; Karen C. Rau^a; Nancy N. Sauer^a

^a Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico

Online publication date: 20 February 2003

To cite this Article Birnbaum, Eva R. , Rau, Karen C. and Sauer, Nancy N.(2003) 'Selective Anion Binding from Water Using Soluble Polymers', *Separation Science and Technology*, 38: 2, 389 – 404

To link to this Article: DOI: 10.1081/SS-120016581

URL: <http://dx.doi.org/10.1081/SS-120016581>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.



SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 2, pp. 389–404, 2003

Selective Anion Binding from Water Using Soluble Polymers

Eva R. Birnbaum,* Karen C. Rau, and Nancy N. Sauer

Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico, USA

ABSTRACT

We investigated water-soluble dendrimers and polymers as ligands for selective anion binding. PAMAM Starburst dendrimers and polyethylenimine have been chemically modified to incorporate new ligands or hydrogen bonding groups at the primary amines. These molecules, along with the unmodified parent compounds, bind arsenate, chromate, and phosphate, even in the presence of competing anions such as chloride. Such systems could potentially be employed for remediation of contaminated water and soils using well-established ultrafiltration technology. Selectivity is achieved through bringing together moieties with a combination of electrostatic and hydrogen bonding capabilities. Total binding capacity for several metalloxyanions has been determined, as well as relative ion selectivity.

Key Words: Anion separation; Dendrimer; PEI; Ultrafiltration.

*Correspondence: Eva R. Birnbaum, Chemistry Division, Analytical Chemistry Sciences (C-ACS) MS K484, Los Alamos National Laboratory, Los Alamos, NM 87545, USA; E-mail: evab@lanl.gov.



INTRODUCTION

The design of ligands for selective metal binding is an important chemical challenge. Metalloanion recognition, in particular, reaches across inorganic and environmental chemistry for applications ranging from sensor development to waste remediation, and is also essential in understanding receptors in biological systems. Anions represent an especially complex target, as they are coordinatively saturated and cannot form covalent bonds to ligands. Many commercially available anion exchange resins make use of electrostatic attraction to retain anions, but such general interactions do not generate selectivity in anion retention. In recent years, a variety of strategies have been utilized to produce anion-specific ligands, sensors, and host molecules, with some notable successes.^[1,2] In the areas of aqueous waste treatment and environmental remediation, design of selective ligand systems for anions is complicated by additional factors. Highly specific ligands are needed that will bind a target species present in very low concentrations and in the presence of much higher concentrations of other anions. Furthermore, binding of target contaminant anions from dilute solution must be combined with methods to remove or concentrate the resultant complexed contaminants from the remaining solution. Finally, the systems must be simple enough to scale for application on a large scale.

Our approach to resolving metal contaminant recovery is through covalent attachment of regenerable ligands to soluble polymeric backbones, as a solution-state analog to ion exchange chromatography.^[3,4] The resulting homogeneous systems should have the accessibility and fast binding kinetics of a molecular ligand while avoiding phase transfer problems that may occur with supported extraction systems such as ion exchange. Separation of soluble polymers (with bound anions) from solution can be accomplished with molecular sieving techniques such as ultrafiltration, which has been demonstrated for a wide molecular weight range of functionalized metal-binding polymers.^[5] For example, we have found that polyethyleneimine (PEI)-based polymers can be used to effectively remove lead from soils^[3] or to concentrate toxic metals or actinides from solution.^[6] While the use of polymeric extractants in combination with ultrafiltration is well established by several groups for simple cation separation and recovery, fewer examples exist for anionic species.^[7] In general, these types of extraction studies have relied on large, flexible soluble polymer systems for metal cation binding.

In this report, we describe the synthesis of modified polyethyleneimine (PEI) and Starburst PAMAM dendrimer complexes that selectively remove oxyanions from aqueous solution. These molecules, along with the parent PEI and PAMAM 4.0 compounds, bind arsenate, chromate, and phosphate, even in



Selective Anion Binding

391

the presence of competing anions such as chloride. The more flexible PEI systems have higher overall anion capacity, but the rigid dendrimer systems have higher selectivity for the oxyanions with respect to competition from chloride. We believe that selectivity is achieved through bringing together moieties with a combination of electrostatic and hydrogen bonding capabilities. These interactions are analogous to the binding types that generate high specificity in anion binding in enzyme systems.^[8]

EXPERIMENTAL

Materials and Methods

PEI was obtained from BASF and purified by ultrafiltration (10K cutoff filter) prior to use to remove low molecular weight fractions. Starburst PAMAM dendrimers (generation 3.0, 3.5, and 4.0) were obtained from Aldrich and used as received. Other chemicals were obtained from Aldrich and used as received. ICP-AES determinations were performed on a Varian Liberty 220. Proton NMR measurements were obtained on a 300-MHz Varian spectrometer with a multinuclear probe (121.4 MHz for ³¹P); all chemical shifts are reported in ppm. Phosphorous spectra were obtained using an external 85% phosphoric acid reference.

Synthesis

PAMAM-OH was synthesized by reaction of PAMAM 4.0 starburst dendrimer with bromoethanol. Bromoethanol was added (20% based on the 64 primary amines on the dendrimer) to a 10% (by weight) solution of the dendrimer in methanol and refluxed overnight. After refluxing overnight and cooling, an equal amount of water was added and the solution was diafiltered through a 10K Amicon ultrafiltration unit to remove unreacted bromoethanol and HBr produced in the coupling reaction. After ultrafiltration, the solution was removed and the polymer redissolved in water to give a known concentration (by weight) solution. PEI-OH was prepared by a similar reaction in ethanol. Bromoethanol was added to an ethanol solution of PEI and refluxed over night. The solution was then sparged to remove HBr, and the solution ultrafiltered to remove unreacted bromoethanol. A proton NMR showed a defined triplet at 3.7 ppm (dendrimer) or a broad resonance at 3.6 ppm (PEI) from the $-\text{CH}_2\text{CH}_2\text{OH}$ protons. This was integrated relative to the total dendrimer backbone protons (2.4 to 3.4 ppm) or polymer backbone



(2.5 to 3.1 ppm) to determine the amount of modification. Eighteen percent of the primary amines in PAMAM-OH were modified.

To synthesize PAMAM-PZ, a solution of PAMAM 4.0 in DMF was prepared and reacted with 2-carboxy pyrazine (5 mol% relative to the 64 primary amine sites on the dendrimer) dissolved in DMF. An equimolar amount of the coupling agent, dicyclohexylcarbodiimide (DCC) was added and the solution stirred until all compounds had dissolved. The reaction was heated (below reflux) until a clear solution was obtained and then cooled. The polymer was filtered through a 10K molecular weight cutoff Amicon filtration system, adding methanol and then water as the volume decreased, until a fivefold excess of solution had been filtered. The methanol filtration was necessary to remove DCU (the byproduct from the coupling reaction) from the solution. Proton NMR was used to determine the degree of modification: 5% in the DCC catalyzed condensation of dendrimer with 2-carboxy-pyrazine. PEI-PZ: 8.98 (s) 8.60 (s) ppm that integrate at a 1:2 ratio; these integrate against the backbone broad resonances at 2.5 to 3.1 ppm. A proton NMR of PAMAM-PZ showed resonances for the three pyrazine protons at 9.1, 8.7, and 7.9 ppm. These could be integrated against the total dendrimer backbone protons to determine the amount of modification.

Capacity Studies

The molar capacity of each dendrimer or polymer was determined in the presence of an excess of anion. A solution of 5-mg dendrimer and 1300 ppm of anion (from the sodium salt) was adjusted to pH 7 and was mildly shaken for 24 hours at room temperature. A portion of each solution was filtered through a Centricon filter with a 3000 molecular weight cutoff, such that the dendrimer (and any bound anion) remained in the retentate. The total metal concentration and the concentration of the permeate, which represents the unbound metal, were measured by ICP-AES, allowing calculation of the bound metal concentration. The mixed anion experiments were conducted with all three analytes at 1300 ppm (based on anion). Polymer studies were conducted in an identical fashion, except that a 10,000 molecular weight cutoff Centricon was used. All results are the average of three or more trials.

Chloride competition studies were conducted using chromate or phosphate as the target anion. Solutions of 5-mg dendrimer and 0.03 M phosphate were prepared and filtered as described previously. To investigate competition effects at lower loading levels, solutions of 5-mg dendrimer (or polymer) and 50 ppm of chromate were allowed to equilibrate in the presence

of zero, 50 ppm, or 5000 ppm of NaCl for 24 hours. The solutions were filtered as described previously, and the chromium concentrations in the original solutions and permeates were determined by ICP-AES.

RESULTS AND DISCUSSION

Single Anion Capacity

Studies were conducted in tandem with PEI and Starburst PAMAM dendrimer derivatives. Polyethyleneimine, with a base repeat unit of $-\text{CH}_2\text{CH}_2\text{NH}-$, and the PAMAM dendrimer, which is based on a *N*-(ethylamino)-propionamide repeating unit ($\text{CH}_2\text{CH}_2\text{CONHCH}_2\text{HC}_2\text{NH}_2$), were chosen as our base molecules for several reasons. The net positive charge of the dendrimer or polymer in neutral water provides an electrostatic attraction for anion binding. The primary amine sites on either system are accessible to solution and will readily undergo chemical modification. These amines can provide either sites for anion binding, or a reactive site to attach a potentially more anion-selective ligand. Both molecules are large enough to be retained by an ultrafiltration membrane, allowing simple separation of bound anions from the remaining solution. A comparison of the polymer, which is a highly crosslinked, amorphous molecule with potential binding sites randomly located throughout, and the dendrimer, which is a rigid, well-characterized molecule with amines ordered on the periphery, will yield information on the relationship between structure and anion binding.

As shown in Fig. 1, the primary amines of each molecule were modified with different ligands to provide three types of hydrogen bonding interactions with anions. We chose ligands that would provide different types of hydrogen bonding groups in an attempt to explore the subtleties of such interactions. By varying the amount of reactant added, different levels of functionalization could be achieved. The amount of functionalization was verified by proton NMR. However, increasing the amount of covalently attached ligand, especially in the dendrimer systems, often reduced the solubility of the systems in water, so most binding studies were conducted with polymers or dendrimers with very low levels of functionalization. This also reduced the potential for quaternation of the interior amine groups; at low levels of reactants, reaction at the primary amine sites would be highly favored for both kinetic and accessibility reasons.

The maximum anion capacity of the dendrimers and polymers was measured in the presence of an excess of anion. The dendrimer or polymer

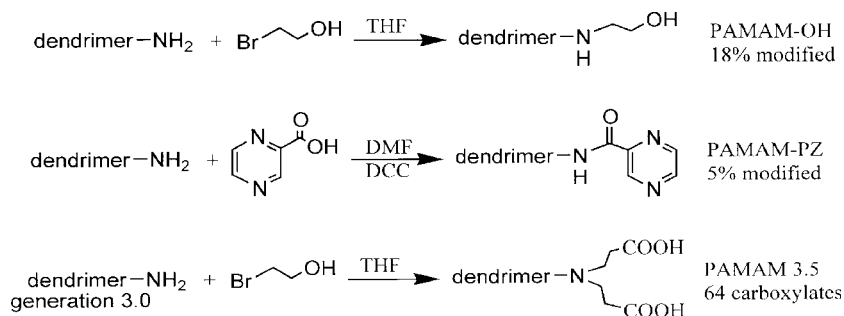


Figure 1. Synthetic scheme for the three modified dendrimers used for anion binding experiments. The polymers were prepared in an analogous fashion.

was contacted with a 1300 ppm solution for 24 hours, then filtered. The concentration of the anion in the permeate was determined by ICP-AES, with the remaining anion assumed to be bound to the dendrimer or polymer. Initially, chromate, arsenate, and phosphate capacities were determined from the sodium salts at pH of 7 (Table 1). Despite the lack of covalent attachment of the anion to the dendrimer, these capacities are of similar magnitude to those of cations,^[3] such as lead or cadmium, with up to 2.07 mmol of anion bound per g of dendrimer or 6.25 mmol of anion per g of polymer. This capacity, though unoptimized with respect to the amount of functionalization of the polymer or of binding conditions, is of similar magnitude to that of some common ion exchange resins.^[9] In contrast, the anionic carboxylate

Table 1. Molar capacity of modified dendrimer complexes and polymers for oxyanions in single anion experiments.

Single anion capacities polymer	Molar capacity (mmol ion/g dendrimer)		
	CrO ₄	AsO ₄	PO ₄
PAMAM 4.0	1.99	1.74	1.62
PAMAM-OH	2.39	1.28	2.07
PAMAM-PZ	1.17	1.08	0.40
PEI	4.13	4.91	6.25
PEI-OH	2.53	3.04	3.93
PEI-PZ	1.79	1.70	2.03

Selective Anion Binding

395

derivative, PAMAM 3.5, showed no capacity for any of the anions; not surprisingly, the negative charge from the carboxylate groups on the dendrimer periphery prohibited binding. The 24-hour contact time used in these experiments was far greater than required; experiments run for 30 minutes or 48 hours gave statistically identical results, indicating that equilibrium is reached quickly in these systems.

Total capacities are higher in each case for the PEI-derivative relative to the similarly modified dendrimer. Further, the capacity of PEI was significantly higher than that of the PEI-derivatives. The unmodified PEI polymer has both electrostatic and hydrogen bonding capacity in both the backbone and the primary amines; it appears that rendering the primary amine sites to $-OH$ or pyrazine groups simply diminished the ability of the polymer to retain anions upon ultrafiltration. In the dendrimers, the substitution of a primary amine for a hydroxyl group did not drop the capacity. Total anion capacity in the dendrimers was similar for PAMAM 4.0 and PAMAM-OH, with both being higher than that of PAMAM-PZ.

The relative selectivity of each polymer or dendrimer is not based on the modifications but on the backbone. While the dendrimers have the highest capacity for chromate, the PEI-derivatives have a slightly higher capacity for phosphate relative to the other anions. The selectivity in the dendrimers is primarily an electrostatic effect. At pH 7, chromate is predominately CrO_4^{2-} , whereas the other species are approximately equally in the mono- and di-protonated forms (HMO_4^{2-} and $H_2MO_4^-$, respectively). This effect should be offset somewhat by the higher formal charge on the central atom of chromate.

The PEI selectivity for phosphate may be due to cooperation of binding sites on the polymer. Unlike the dendrimer, which is fairly rigid, the charged sites and hydrogen binding sites on the amorphous PEI-derivatives could orient into more favorable positions based on the size of the target anion. The size of the anions increases from $HPO_4^{2-} < HAsO_4^{2-} < CrO_4^{2-}$,^[10] which mirrors the observed selectivity trend in the PEI-derivatives, with the smallest anion having the highest affinity.

Proton NMR experiments did not elucidate if anions were binding to the interior or exterior of the dendrimers. A potential binding mode in the dendrimers would be in cyclic defect sites that have been observed in the dendrimer cores.^[11,12] We were unable to detect such sites by proton NMR. If such sites are present at low concentrations, the effect would be equivalent for all the dendrimers studied, as all were synthesized from the same base molecule. In this case, the relative anion selectivity between the dendrimers is obviously unaffected. Also, as the groups added by chemical modification of the dendrimers were readily observed by NMR, even at very

low levels, we do not believe that defect sites play a large role in the interactions of the dendrimers with anions.

Attempts to probe the anion environment directly using NMR were unsuccessful. The addition of ammonium phosphate to a dendrimer solution was followed by ^{31}P -NMR. As long as the phosphate solution was buffered, so that so pH change occurred upon addition to the dendrimer solution, no change in the phosphate resonance was observed. The phosphate resonance was similar to that of ammonium phosphate in the absence of dendrimer, indicating that interactions between the dendrimer and phosphate must be relatively weak and not perturb the electronic structure of the central atom of the oxyanions.

Mixed Anion Capacity

The capacity of the polymers and dendrimers was also measured from a mixture of the anions, to see if capacity or selectivity changed under these conditions. The PEI-derivatives lose much of their capacity, down more than 50% from the single anion experiments (Table 2). This suggests that the interactions of anions with PEI are primarily electrostatic and, as such, are disrupted at higher ionic strength. The dendrimers retain their total high capacity; if a mixture of oxyanions is present, total ion capacity for PAMAM 4.0 and PAMAM-OH remains almost unchanged (see Table 2). The capacity of PAMAM-PZ actually increases up to a level similar to the other dendrimers. The lower capacity of PAMAM-PZ in the single anion experiments suggests that unfavorable intermolecular interactions exist. The pyrazine is either blocking potential binding sites on the dendrimer surface, or

Table 2. Molar capacity of modified dendrimer complexes and polymers for oxyanions in mixed anion experiments.

Mixed anion capacities polymer	Molar capacity (mmol ion/g dendrimer)			
	CrO ₄	AsO ₄	PO ₄	Total capacity
PAMAM 4.0	0.88	0.48	0.38	1.74
PAMAM-OH	0.95	0.63	0.54	2.12
PAMAM-PZ	0.81	0.51	0.34	1.66
PEI	1.39	0.67	0.68	2.74
PEI-OH	0.84	0.28	0.42	1.54
PEI-PZ	0.59	0.58	0.48	1.65

Selective Anion Binding

397

restricting access to the interior of the dendrimer. One possible hydrogen-bonding mode is shown in Fig. 2. Such interactions are disrupted at higher ionic strength, allowing the oxyanions access to binding sites on the pyrazine-modified dendrimer. Similar aggregation of polymers in solution, particularly hydrogen-bonding polymers such as PEI and polyacrylic acid is well documented.^[13] The pyrazine did not give the desired selectivity, but does indicate the importance of considering hydrogen-bonding interactions in designing an anion-selective system.

Although the relative selectivity among the dendrimers remains the same, the polymers reveal a preference for chromate in the mixed anion experiments. The anticipated selectivity for phosphate based on the single anion experiments is not borne out under the higher ionic strength conditions. The phosphate sites may be weaker interactions, and in the presence of chromate, the electrostatic attraction of the polymer for higher charged ion is the dominating effect.

Competition Experiments

The selectivity for oxyanion binding in the presence of chloride was also investigated. Phosphate binding in the presence of an equal concentration of NaCl (0.03 M) was relatively unaffected in the case of PAMAM 4.0 and only slightly decreased with PAMAM-OH (Fig. 3). As in the mixed anion

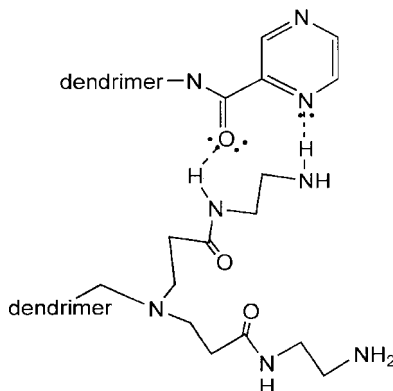


Figure 2. Potential hydrogen bonding interactions between the dendrimer backbone and the pyrazine ligand.

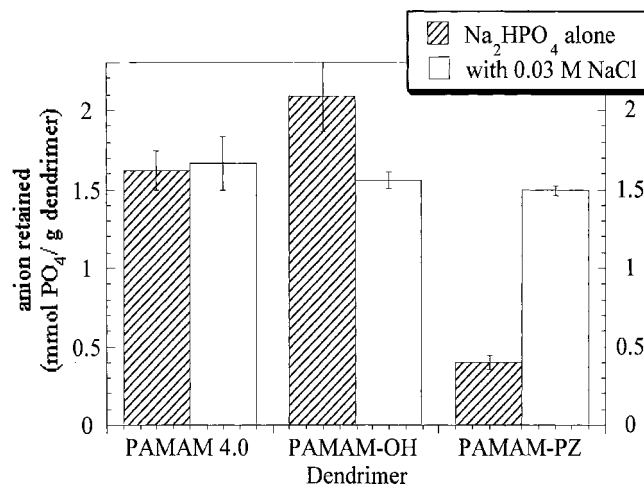


Figure 3. Phosphate capacity of each dendrimer in the presence of 0.015 M Na₂HPO₄ (stripes), or in the presence of phosphate and a twofold excess of NaCl. The error bars show the standard deviation of the individual trials. The chloride does not compete significantly for binding sites on the dendrimers (4.0 and -OH), but binding of phosphate dramatically increases on the pyrazine derivative. The addition of chloride appears to open up binding sites on the pyrazine dendrimer.

experiments, the capacity of PAMAM-PZ dramatically increased (back to the average value for the other dendrimers), again suggesting that this dendrimer has strong intermolecular interactions, which limit access to the dendrimer, and are significantly reduced by increasing ionic strength. Further evidence for such a low amount of functionalization restricting binding sites on the dendrimer comes from the testing of PAMAM-PZ at 2.5% functionalization. This dendrimer bound phosphate at a capacity between that of the base 4.0 and the 5% functionalized PAMAM-PZ. Together these results indicate that the dendrimer backbone, like the PEI backbone, drives the anion binding chemistry.

In order to test competition effects at lower total loadings, the effect of different chloride concentrations on chromate binding to the dendrimers and polymers was investigated. For the dendrimers (Fig. 4), the binding capacity was not changed within experimental error between no chloride and 50 ppm of chloride, at roughly 90–95% bound metal for all the dendrimers. However, at a 100-fold excess of competing ion, chromate binding dropped significantly, to just below 50%, for all dendrimers. Despite the large excess of chloride,

Selective Anion Binding

399

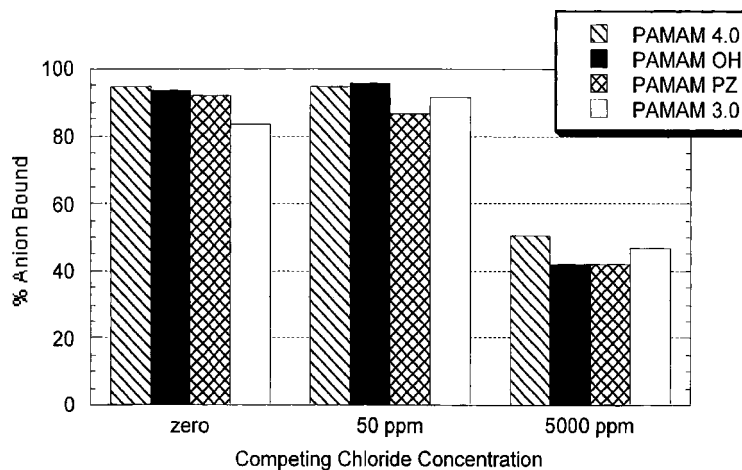


Figure 4. Chromate capacity of each dendrimer with an initial concentration of 50 ppm Cr and increasing chloride concentrations of 50 and 5000 ppm.

significant capacity remained in the dendrimer. At low metalloxyanion loadings, it appears that the modifications of the dendrimer become unimportant, and the majority of interactions occur between the anions and the dendrimer backbone. Interestingly, the generation 3.0 dendrimer, with only 32 primary amine sites, was almost identical in behavior to that of the 4.0, indicating that the dendrimer is not saturated at these relatively low loadings.

The polymers showed a different trend with increasing chloride concentration (Fig. 5). As in the competition experiments, the total capacity of the polymers was lower, but was almost completely unaffected by the presence of chloride. Capacity was at approximately 70% of the available chromate regardless of the competing chloride concentration.

A particularly important environmental problem is the recovery of small amounts of contaminants from dilute natural or process waters. The dendrimer systems were also able to complex relatively dilute streams of oxyanions with subsequent concentration by ultrafiltration. For example, from a solution of 75 ppm chromate, a single ultrafiltration with PAMAM-OH removed over 94% of the metal, resulting in a permeate chromate concentration below the U.S. Resource Conservation and Recovery Act (RCRA) action level of 5 ppm for waste waters. This corresponds to a K_d of 10,300.^[14] The high concentration of chromate in the resulting solutions did not appear to cause degradation of the dendrimers under these conditions, as no dichromate was

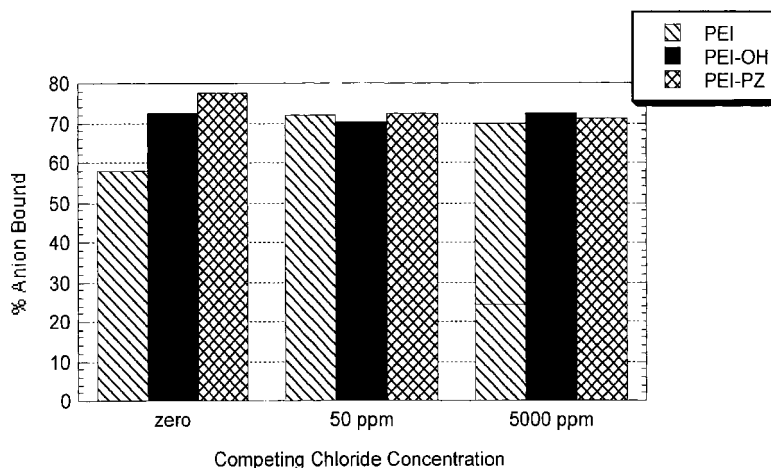


Figure 5. Chromate capacity of each polymer with an initial concentration of 50 ppm Cr and increasing chloride concentrations of 50 and 5000 ppm.

observed by UV–Vis spectroscopy. Also, UV–Vis spectra of dendrimer-chromate or polymer-chromate (1100 ppm Cr as CrO_4) solutions after several weeks showed no reduced chromium species.

The combination of hydrogen bonding and electrostatic interactions are designed to give a specific site for an oxyanion. For example, crystal structures show that hydrogen bonds are important in the encapsulation of guests into different cyclic macrocycles.^[15–17] Larger macrocycles have also been prepared that use hydrogen bond donors similar in structure to those found in the dendrimers and polymers described here, with C_3 symmetry to bind tetrahedral anions such as phosphate and sulfate.^[18] As the dendrimers and polymers are not so rigid, we instead suggest formation of transitory binding pockets for the anions in solution. Such pockets are formed by selective anion-binding proteins,^[8] and are proposed to exist in dendrizymes (dendrimer complexes for catalysis that mimic enzymes).^[19] The ability to bind the oxyanions even in the presence of excess halide suggests that the dendrimers may form such pockets in solution.

CONCLUSION

We demonstrated that water-soluble dendrimer and polymer systems modified with hydrogen bonding groups have significant capacity for

**Selective Anion Binding****401**

oxyanions (arsenate, chromate, phosphate) in aqueous solutions. Ultrafiltration of these solutions results in concentration of the anions in the retentate and a clean permeate. The precise mechanism of binding was not determined, although a surface interaction similar to that observed between dendrimers and the photoactive $\text{Ru}(4, 7-(\text{SO}_3\text{C}_6\text{H}_5)_2\text{-phen})_3^{4-}$ is believed to occur.^[20] The majority of the binding in both the polymers and the dendrimers is based on the backbone, as modification either lowered the total capacity or had no effect. ³¹P-NMR studies indicate that the interaction between the phosphate and the dendrimers is weak, as the phosphate resonance is not shifted in the presence of any of the dendrimers. Repeated ultrafiltration with neutral pH water also slowly strips the anion from the dendrimer, a second indication that the binding interactions are not strong. The regenerability of these systems will be explored through a rinse with a highly basic solution, competitive binding of the anion to form a molecular complex, or reduction of the anion. Further investigations would be required to explore the effects of percentage of functionalization, pH, dendrimer type or generation, and to elucidate more specific information on the anion binding modes.

ACKNOWLEDGMENTS

Brandy Duran and Deborah Ehler are thanked for their assistance with ICP analysis. Andrew Trout is acknowledged for assistance in manuscript preparation. This work was funded by the Los Alamos National Laboratory Directed Research and Development Program. LAUR 98-5251, 01-4876. LANL is operated by the University of California for the U.S. Department of Energy under Contract W-7405-ENG-3.

REFERENCES

1. Molecules including crown ethers, cryptates, calixarenes, and expanded porphyrins have been well studied, for example see: Lehn, J-M. Cryptates: chemistry of macropolycyclic inclusion complexes. *Acc. Chem. Res.* **1978**, *11* (2), 49–57; Lehn, J-M. Supramolecular chemistry: scope and perspectives molecules, supermolecules, and molecular devices. *Ang. Chemie, Int. Ed. Eng.* **1988**, *27* (1), 89–112; Izatt, R.M. Review of selective ion separations at BYU using liquid membrane and solid phase extraction procedures. *J. Inclusion Phenom. Recognit. Chem.* **1997**, *29* (3–4), 197–220; Boudon, S.; Decian, A.; Fischer, J.;

- Hosseini, M.; Lehn, J.-M.; Wipff, G. Structural and anion coordination features of macrocyclic polyammonium cations in the solid, solution and computational phases. *J. Coord. Chem.* **1991**, *23* (1–4), 113–135; Shionoya, M.; Furuta, H.; Lynch, V.; Harriman, A.; Sessler, J.L. Diprotonated sapphyrin: a fluoride selective halide anion receptor. *J. Am. Chem. Soc.* **1992**, *114* (4), 5714–5722; Antoniesse, M.M.G.; Reinhoudt, D.N. Neutral anion receptors: design and application. *Chem. Comm.* **1998**, *4*, 443–448; Choi, K.H.; Hamilton, A.D. Selective anion binding by a macrocycle with convergent hydrogen bonding functionality. *J. Am. Chem. Soc.* **2001**, *123* (10), 2456–2457.
- Beer, P.D. Transition-metal receptor systems for the selective recognition and sensing of anionic guest species. *Acc. Chem. Res.* **1998**, *31*, 71–80; Gale, P.A. Anion receptor chemistry highlights from 1999. *Coord. Chem. Rev.* **2001**, *213*, 79–128; Gale, P.A. Anion coordination and anion-directed assembly: highlights from 1997 and 1998. *Coord. Chem. Rev.* **2000**, *199*, 181–233; Beer, P.D.; Gale, P.A. Anion recognition and sensing: the state of the art and future perspectives. *Angew. Chem. Int. Ed. Eng.* **2001**, *40* (3), 487–517.
 - Smith, B.F.; Robison, T.W.; Sauer, N.N.; Ehler, D.S. Water-Soluble Polymers for Recovery of Metals from Soils, Sludges, or Wastes. US Patent 5,928,517, 1999.
 - Beauvais, R.A.; Alexandratos, S.D. Polymer-supported reagents for the selective complexation of metal ions: an overview. *React. Funct. Polym.* **1998**, *36* (2), 113–123; Smith, S.D.; Alexandratos, S.D. Ion-selective polymer-supported reagents. *Solvent Extract. Ion Exch.* **2000**, *18* (4), 779–807; Smith, B.F.; Gibson, R.R.; Jarvinen, G.D.; Robison, T.W.; Schroeder, N.C.; Stalnaker, N.D. Preconcentration of low levels of americium and plutonium from waste waters by synthetic water-soluble metal-binding polymers with ultrafiltration. *J. Radioanalytical Nucl. Chem.* **1998**, *234* (#1–2), 225–229.
 - Geckeler, K.; Lange, G.; Eberhardt, H.; Bayer, E. Preparation and application of water-soluble polymer–metal complexes. *Pure Appl. Chem.* **1980**, *52* (7), 1883–1905; Geckeler, K.; Shkinev, V.M.; Spivakov, B.Y. Liquid-phase polymer-based retention LPR: a new method for selective ion separation. *Sep. Purif. Methods*, **1988**, *17* (2), 105–140; Geckeler, K.E.; Volchek, K. Removal of hazardous substances from water using ultrafiltration in conjunction with soluble polymers. *Environ. Sci. Technol.* **1996**, *30* (3), 725–734.
 - Vanderberg, L.A.; Foreman, T.M.; Attrep, M., Jr.; Brainard, J.R.; Sauer, N.N. Treatment of heterogeneous mixed wastes: enzyme degradation of

- cellulosic materials contaminated with hazardous organics and toxic and radioactive metals. *Environ. Sci. Technol.* **1999**, 33 8, 1256–1262.
7. Geckeler, K.E.; Weingartner, K.; Bayer, E. In *Polymeric Amines and Ammonium Salts*; Goethals, E.J., Ed.; Pergamon Press: New York, 1979; 277–286.; Shtereva, G., Dytnersky, Y., Khozhainov, Y., Zhilin, Y. In *Proceedings of the Fourth National Conference on Membrane Methods*, Moscow, May 27–29, 1987; Vol. 4, 52–55; Geckeler, K.E.; Bayer, E. A new method for anion-exchange using soluble polymers. *Naturwissenschaften* **1988**, 75 (4), 198–199.
 8. Luecke, H.; Quioco, F.A. High specificity of a phosphate-transport protein determined by hydrogen bonds. *Nature* **1990**, 347 6291, 402–406.
 9. Sybron Chemicals Inc. IONAC[®] C-250 resin has a capacity of 2.7 meq/g, Dow Chemicals DOWEX[®] SBR resin capacity is 1.4 meq/L. Data from the respective company web pages.
 10. Marcus, Y.; Loewenschuss, A. Standard entropies of hydration of ions. *Annu. Rep. Prog. Chem. Sect. C.: Phys. Chem., Roy. Chem. Soc. (London)* **1985**, 81–135.
 11. Tomalia, D.A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. A new class of polymers: Starburst-dendritic macromolecules. *Polym. J.* **1985**, 17 (1), 117–132.
 12. Tomalia, D.A.; Durst, H.D. Genealogically directed synthesis: Starburst cascade dendrimers and hyperbranched structures. *Top. Curr. Chem.* **1993**, 165, 193–313.
 13. Lapin, V.V.; Misyutina, T.I.; Sokolova, B.I.; Drobosyuk, V.M.; Shpenzer, N.P.; Talmud, S.L. Aggregation of polyethylenimine in aqueous solution. *J. Appl. Chem. USSR*. **1979**, 52, 205–206; Masse, P.; Choe, T.B.; Verdier, A. Separation of Cu(II)–Ni(II) by a complexation–ultrafiltration method. *Ann. Chim.* **1987**, 77 (11–1), 925–944; Horn, D. In *Polymeric Amines and Ammonium Salts*; Goethals, E.J., Ed.; Pergamon Press: New York, 1979; 334–354; Volchek, K.; Krentsel, E.; Zhilin, Y.; Shtereva, G.; Dytenersky, Y. Polymer binding ultrafiltration as a method for concentration and separation of metals. *J. Membr. Sci.* **1993**, 79 (2–3), 253–272.
 14. K_d is defined as (total bound metal/total free metal)*(mL solution volume/g dendrimer).
 15. Turner, B.; Shterenberg, A.; Kapon, M.; Suwinska, K.; Eichen, Y. Selective anion binding and solid-state host–guest chemistry of an extended cavity Calix[6]pyrrole. *Chem. Commun.* **2001**, 01, 13–14.



16. Cafeo, G.; Kohnke, F.H.; La Torre, G.L.; White, A.J.P.; Williams, D.J. The complexation of halide ions by Calix[6]pyrrole. *Chem. Commun.* **2000**, 13, 1207–1208.
17. Bencini, A.; Bianchi, A.; Garcia-Espana, E.; Giusti, M.; Mangani, S.; Micheloni, M.; Orioli, P.; Paoletti, P. Anion coordination chemistry 2. Electrochemical, thermodynamic, and structural studies on super-complex formation between large polyammonium cycloalkanes and the 2 complex anions hexacyanoferrate(II) and hexacyanocobaltate(III). *Inorg. Chem.* **1987**, 26 (23), 3902–3907.
18. Choi, K.; Hamilton, A. Selective anion binding by a macrocycle with convergent hydrogen bonding functionality. *J. Am. Chem. Soc.* **2001**, 123 (10), 2456–2457.
19. Brunner, H. Dendrzymes: expanded ligands for enantioselective catalysis. *J. Organomet. Chem.* **1995**, 500 (1–2), 39–46.
20. Schwarz, P.F.; Turro, N.J.; Tomalia, D.A. Interactions between positively charged starburst dendrimers and $\text{Ru}(4,7\text{-(SO}_3\text{C}_6\text{H}_5)_2\text{-phen)}_3^{4-}$. *J. Photochem. Photobiol A—Chem.* **1998**, 112 (1), 47–52.

Received December 2001

Revised May 2002