

Dendritic Chelating Agents. 2. U(VI) Binding to Poly(amidoamine) and Poly(propyleneimine) Dendrimers in Aqueous Solutions

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Chelating agents are widely employed in many separation processes used to recover uranyl [U(VI)] from contaminated aqueous solutions. This article describes an experimental investigation of the binding of U(VI) to poly(amidoamine) [PAMAM] and poly(propyleneimine) [PPI] dendrimers in aqueous solutions. We combine fluorescence spectroscopy with bench scale ultrafiltration experiments to measure the extent of binding and fractional binding of U(VI) in aqueous solutions of these dendrimers as a function of (i) metal–ion dendrimer loading, (ii) dendrimer generation, (iii) dendrimer core and terminal group chemistry, and (iv) solution pH and competing ligands (NO_3^- , PO_4^{3-} , CO_3^{2-} , and Cl^-). The overall results of this study suggest that uranyl binding to PAMAM and PPI dendrimers in aqueous solutions involves the coordination of the UO_2^{2+} ions with the dendrimer amine, amide, and carboxylic groups. We find significant binding of U(VI) to PAMAM dendrimers in (i) acidic solutions containing up to 1.0 M HNO_3 and H_3PO_4 and (ii) in basic solutions containing up to 0.5 M Na_2CO_3 . However, no binding of U(VI) by PAMAM dendrimers is observed in aqueous solutions containing 1.0 M NaCl at pH 3.0. These results strongly suggest that PAMAM and PPI dendrimers can serve as high capacity and selective chelating ligands for U(VI) in aqueous solutions.

Introduction

The mining and processing of uranium ores and the production, reprocessing and disposal of uranium fuel rods generate a broad range of liquid effluents (1–4). The treatment of these contaminated wastewater streams is a key component of the uranium nuclear fuel cycle (1–4). Uranyl [U(VI)] is the most stable uranium species under the typical oxidizing conditions encountered in the treatment of aqueous effluents (3). Solvent extraction (SE), ion exchange (IX), and sorption are the most widely used processes to recover uranyl from aqueous solutions (2–4). The PUREX SE process has become the de facto technology for recovering uranium species from

concentrated nitric acid solutions used in the processing of spent nuclear fuel rods (2). While sorption has been primarily employed in nuclear waste management to treat aqueous waste streams containing low concentration of U(VI) (2), IX has been used to (i) recover uranyl from aqueous solutions and high level radioactive wastes and (ii) extract uranium species from concentrated nitric acid solutions in spent nuclear fuel processing facilities. Although SE and IX are well-established and proven uranium separation technologies, their lack of selectivity, low efficiency, and environmental impact are major drawbacks (2–4). A number of alternative uranium separation technologies are currently being investigated including extraction in room-temperature ionic liquids, magnetic separation and membrane filtration (2). The dendrimer filtration process developed by Diallo (5, 6) could provide a viable technology to recover actinides such as U(VI) from aqueous solutions once suitable and cost-effective dendritic chelating ligands have been identified.

As a first step toward the development of high capacity, selective, recyclable, and low cost dendritic chelating for actinides, we initially focus on the characterization of U(VI) binding to dendrimers in aqueous solutions. Dendritic macromolecules, which include hyperbranched polymers, dendrigraft polymers, dendronized linear polymers, dendrons, and dendrimers are emerging as ideal platforms for the development of a new generation of high capacity selective and recyclable ligands for water treatment (5, 6). They consist of 3-D globular compounds with three covalently bonded components (7): a core, interior branch cells, and terminal branch cells. These soft nanomaterials, with sizes in the range of 1–20 nm, can be used as high capacity and recyclable chelating agents for a variety of metal ions including Cu(II), Ni(II), Co(II), Pd(II), Pt(II), Zn(II), Fe(III), Ag(I), and Au(I) (8–15). While significant research efforts have been devoted to the aqueous complexation of transition metal ions with dendrimers (8–15), binding of actinides such as U(VI) to dendrimers has received little attention (16).

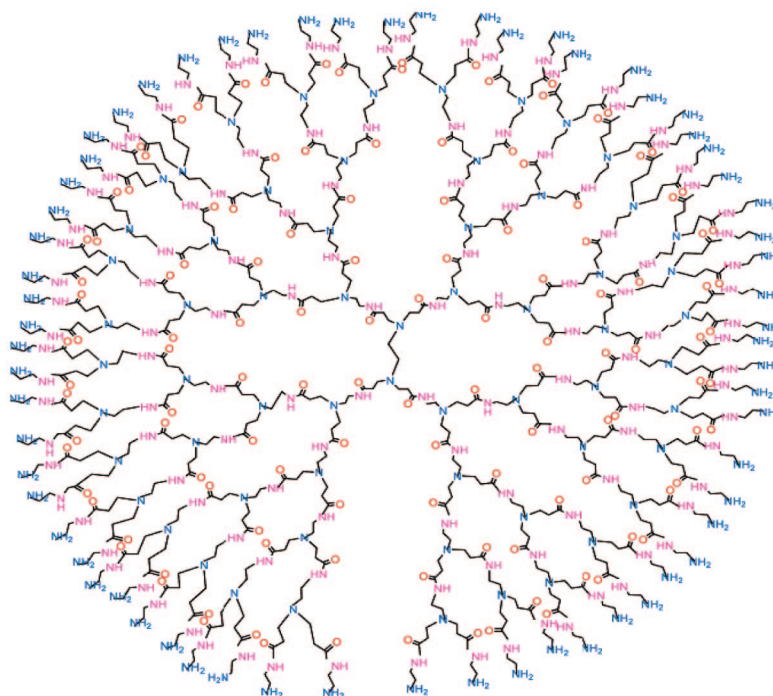
U(VI) is a “hard” Lewis acid and thus forms strong complexes with “hard” Lewis bases including chloride (Cl^-), inorganic ligands with O^- donors (e.g., sulfate, carbonate, phosphate and nitrate) and organic ligands with O and N donors (e.g., amide and amines) (3), (17–22). Poly(amidoamine) [PAMAM] and poly(propyleneimine) [PPI] dendrimers (Figure 1) provide good model systems for probing the aqueous coordination chemistry of U(VI) with dendritic macromolecules. PAMAM dendrimers possess amide, tertiary, and primary amine groups arranged in regular “branched upon branched” patterns, which are displayed in geometrically progressive numbers as a function of generation level. Conversely, PPI dendrimers have tertiary amine and primary amine groups linked by propyl chains. To the best of our knowledge, no follow-up investigation has been published since Ottaviani et al. (16) showed the unexpectedly efficient and selective binding of U(VI) to a generation 6 (G6-NH₂) PAMAM dendrimer with ethylene diamine (EDA) core and terminal NH₂ groups. However, no data on the U(VI) binding capacity of PAMAM and other dendrimers were collected in the study by Ottaviani et al. (16). For the most part, they only provided indirect evidence of U(VI) binding to a G6-NH₂ PAMAM dendrimer. They concluded that PAMAM dendrimers bind U(VI) ions in aqueous solutions when transmission electron microscopy (TEM) images showed the disappearance of uranyl-stained dimyristoylphosphatidylcholine (DMPC) liposomes in the presence of a G6-NH₂ PAMAM dendrimer. The liposomes became only

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A. G4-NH₂ PAMAM Dendrimer



B. G5-NH₂ PPI Dendrimer

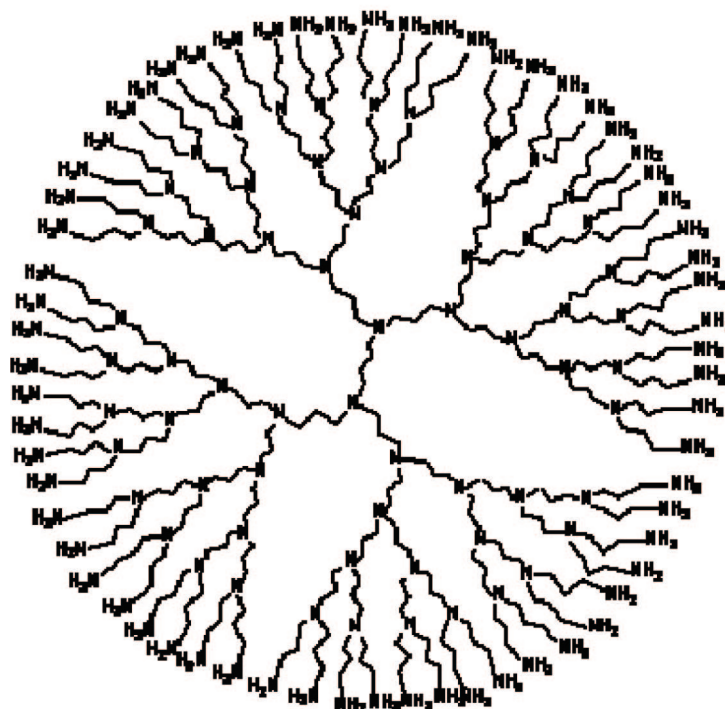


FIGURE 1. 2-D structures of selected PAMAM and PPI dendrimers evaluated in this study: A. G4-NH₂ PAMAM Dendrimer; B. G5-NH₂ PPI Dendrimer.

visible when they were mixed with large amounts (40% by weight) of a negatively charged sodium salt of DMPC at low pH (~4.0) and low dendrimer concentration ($\sim 5.0 \times 10^{-5}$ M). To gain insight into the mechanisms of U(VI) binding to PAMAM dendrimers, Ottaviani et al. (16) subsequently carried out electron paramagnetic resonance (EPR) studies of mixtures of Cu(II) + U(VI) in aqueous solutions of the G6-NH₂ PAMAM dendrimer and showed that uranyl ions compete favorably with copper ions for the amine groups of the PAMAM dendrimer.

Despite these advances, our understanding of uranyl uptake by dendritic chelating agents in aqueous solutions is very limited. A systematic investigation of the effects of solution pH, background electrolyte concentration, and metal-ion dendrimer loading on U(VI) complexation with dendrimers such as PAMAM has yet to be carried out. From a more fundamental point of view, little is known of the effects of dendrimer generation and terminal group chemistry on the uranyl binding capacity and selectivity of dendrimers in aqueous solutions. This article discusses the binding of U(VI)

TABLE 1. Selected Properties of the PAMAM and PPI Dendrimers Evaluated in this Study

dendrimer	M_{wth}^a	N_{terminal}^b	N_{R3N}^c	N_{amide}^d	$N_{\text{H}_2\text{Obound}}^e$	N_{Ligand}^f	$\text{p}K_{\text{R3N}}^g$	$\text{p}K_{\text{terminal}}^h$
G5-NH ₂ PAMAM	28826	128	126	252	524	758	6.30–6.85	9.23–10.0
G4-NH ₂ PAMAM	14215	64	62	124	201	374	6.30–6.85	9.23–10.0
G3-NH ₂ PAMAM	6909	32	30	60	NA ⁱ	182	6.30–6.85	9.23–10.0
G4-OH PAMAM	14279	64	62	124	NA ⁱ	310	6.30–6.85	> 14.0
G3.5 PAMAM	12931	30	64	60	NA ⁱ	214	6.30–6.85	4.5
G5-NH ₂ PPI	7168	64	62	0	NA ⁱ	126	6.10	9.75

^a M_{wth} : theoretical molecular weight. ^b N_{terminal} : number of terminal groups. ^c N_{R3N} : number of tertiary amine groups. ^d N_{amide} : number of amide groups. Note that each amide group has 2 electron donors: 1 N atom and 1 O atom. ^e $N_{\text{H}_2\text{Obound}}$: number of water molecules that are bound to the G4 and G5 PAMAM dendrimers at neutral pH (~7.0). The estimates are taken from Maiti et al. (23). ^f N_{Ligand} : number of dendrimer N and O ligands; $N_{\text{Ligand}} = N_{\text{terminal}} + N_{\text{R3N}} + 2N_{\text{amide}}$. Note that the OH groups of the G4-OH PAMAM dendrimer do not appear to provide coordination sites for U(VI) ions as suggested by Szabó et al. (18). ^g $\text{p}K_{\text{R3N}}$: $\text{p}K_{\text{a}}$ of dendrimer tertiary amine groups. The $\text{p}K_{\text{a}}$ of the tertiary amine groups were taken from refs 24–27. ^h $\text{p}K_{\text{terminal}}$: $\text{p}K_{\text{a}}$ of dendrimer terminal groups. The $\text{p}K_{\text{a}}$ of the terminal primary amine, hydroxyl and carboxyl groups ($\text{p}K_{\text{NH}_2}$, $\text{p}K_{\text{OH}}$ and $\text{p}K_{\text{COOH}}$) of the dendrimers were taken from refs 24–27. ⁱ NA: not available.

to PAMAM and PPI dendrimers in aqueous solutions. We combine fluorescence spectroscopy with bench scale ultra-filtration experiments to measure the extent of binding and fractional binding of U(VI) to these dendrimers as a function of (i) metal–ion dendrimer loading, (ii) dendrimer generation, (iii) dendrimer core and terminal group chemistry, and (iv) solution pH and competing ligands (NO_3^- , PO_4^{3-} , CO_3^{2-} and Cl^-). The overall results of this study strongly suggest that dendritic macromolecules such as PAMAM and PPI dendrimers can serve as high capacity and selective chelating ligands for U(VI) in aqueous solutions.

Experimental Section

Materials. Uranium atomic absorption standard solution (1000 mg/L in 1.0 wt. % HNO_3) from Sigma-Aldrich was used as source of U(VI). Reagent grade nitric acid (HNO_3), phosphoric acid (H_3PO_4), sodium carbonate (Na_2CO_3) and sodium chloride (NaCl) from Sigma-Aldrich were used as sources of competing ligands (NO_3^- , PO_4^{3-} , CO_3^{2-} and Cl^-). G3-NH₂, G4-NH₂, G5-NH₂, G4-OH, G3.5-COONa PAMAM dendrimers and G5-NH₂ PPI dendrimer in methanol solutions were purchased from Sigma-Aldrich and used as received. Table 1 gives selected properties of the dendrimers evaluated in this study. The number of water molecules bound to the G4 and G5 PAMAM dendrimers were taken from Maiti et al. (23) The $\text{p}K_{\text{a}}$ of the tertiary amine groups ($\text{p}K_{\text{R3N}}$), primary amine, hydroxyl, and carboxyl groups ($\text{p}K_{\text{NH}_2}$, $\text{p}K_{\text{OH}}$ and $\text{p}K_{\text{COOH}}$) of the PAMAM and PPI dendrimers were taken from refs (8) and (24–27), respectively. The extents of protonation of the dendrimer tertiary amine, primary amine, and carboxylic groups are given in Table S1 of the Supporting Information (SI). They were calculated using the Henderson–Hasselbach equation (8, 26). This simplified methodology gives results comparable in accuracy to those obtained using theoretically derived models including a modified Ising model and a multishell microscopic protonation model (24, 25).

Methods and Procedures. For each dendrimer, batch experiments were carried out to determine the extent of binding and fractional binding of U(VI) in aqueous solutions. All experiments were carried at room temperature in 15 mL polypropylene centrifuge tubes. The U(VI) concentration was kept constant at 10 ppm (3.7×10^{-5} M) in all experiments. Aliquots of U(VI), dendrimer stock solution, deionized water or deionized water + competing ligands were added to each tube to prepare 10 mL solutions with a given U(VI)–dendrimer molar ratio. Following Diallo et al. (8), the pH of each solution was adjusted by addition of droplets of concentrated HNO_3 or NaOH solutions. The sealed centrifuge tubes were mixed on a rotary shaker for ~60 min. A 4 mL aliquot was subsequently withdrawn from each equilibrated tube and

transferred into a Millipore Centricon filter with a molecular weight cutoff of 5000 Dalton. The filters were centrifuged for 20 min at 3000 rpm to separate the uranyl-laden dendrimers from the aqueous solutions. The concentrations of uranyl in each centrifuge tube (U_0) and filtrate (U_f) were measured by fluorescence spectrophotometry. Following Gu et al. (28), each sample was diluted 10-fold with a 10 wt % H_3PO_4 solution. The complexation of U(VI) ions with phosphoric acid causes a large enhancement of their fluorescence emission intensity. This provides the basis of a uranyl assay method with a detection limit of ~40 ppb [1.48×10^{-6} M] (28). SI Figure S1 highlights a typical calibration curve used to determine uranyl concentration from the fluorescence emission spectra. All fluorescence emission spectra were collected on a steady-state Fluoromax2 spectrometer (Horiba Jobin Ivon) using an excitation wavelength of 280 nm. The emission spectra were recorded between 480 and 545 nm. The intensity of the emission peak at ~508 nm was used to develop the U(VI) calibration curves (SI Figure S1).

The concentration of uranyl bound to a dendrimer (U_b) (mol/L) was expressed as follows:

$$U_b = U_0 - U_f \quad (1)$$

The extent of binding (EOB) [moles of U(VI) bound per mole of dendrimer], the concentration of dendrimer (C_d) in solution (mol/L) and the fractional binding (FB) were expressed as follows:

$$\text{EOB} = \frac{U_b}{C_d} \quad (2)$$

$$C_d = \frac{m_d}{V_s M_{\text{wd}}} \quad (3)$$

$$\text{FB} = 100 \times \left(\frac{U_b}{U_0} \right) \quad (4)$$

where m_d (g) is the mass of dendrimer in solution, V_s (L) is the solution volume and M_{wd} (g/mol) is the molar mass of the dendrimer (Table 1).

Results and Discussion

Effect of Solution pH on U(VI) Binding to Dendrimers.

Figure S2 of the Supporting Information shows the steady-state fluorescence emission spectra of U(VI) in aqueous solutions of G4-NH₂ and G4-OH PAMAM dendrimers at room temperature and pH 2.0. U(VI) has a long-lived luminescent excited state. In deionized water at pH 2.0, U(VI) ions are present as $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ species that exhibit fluorescence emission spectra with intense peaks and broad bands (18, 29). The luminescence of U(VI) is not quenched by molecular

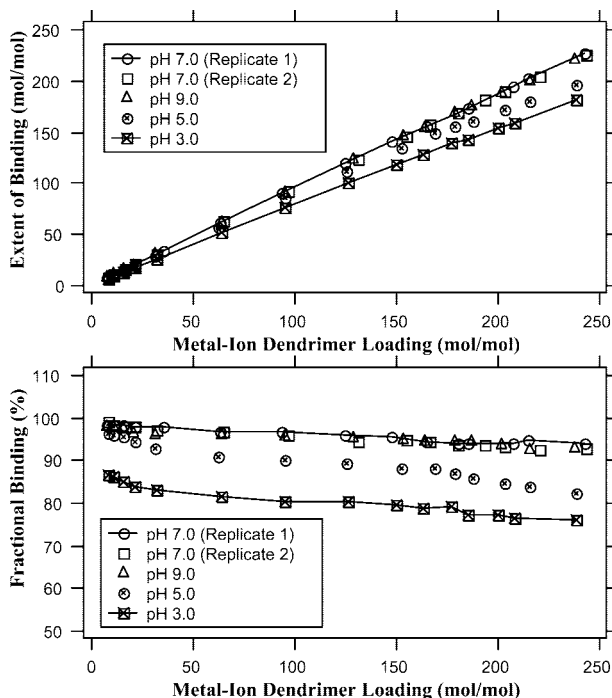


FIGURE 2. Extent of binding and fractional binding of U(VI) in aqueous solutions of H₂ PAMAM dendrimer at room temperature.

oxygen (29). However, complexation of U(VI) ions with organic/inorganic ligands in aqueous solutions causes significant changes in the intensity (e.g., quenching or enhancement), peak position and bandwidth of their fluorescence emission spectra (18, 29). The quenching of the fluorescence of U(VI) in aqueous solutions of the PAMAM dendrimers suggests binding to the dendrimers. Note that the spectral peaks are very broad while their positions remain unchanged in aqueous solutions of the G4-NH₂ and G4-OH PAMAM dendrimers. Thus, they are not readily resolved by standard deconvolution methods used to separate the signals of luminescent complexes from their unbound metal ions in aqueous solutions (18). Because PAMAM and PPI dendrimers are macroligands with a large number of N and O donors (Table 1), the standard Stern–Volmer equation used to estimate the stability constants of complexes of luminescent actinides with small organic ligands (18) is not applicable in this case. Diallo et al. (8) have successfully used the extent of binding (EOB) (i.e., the number of moles of bound metal ions per mole of dendrimer) to quantify cation uptake by dendrimers in aqueous solutions. Figure 2 shows the EOB and FB of U(VI) in aqueous solutions of the G4-NH₂ PAMAM dendrimer. In these experiments, we varied the molar ratio of total uranyl to total dendrimer in solution to prepare samples with a given metal–ion dendrimer loading. Replicate measurements were carried out in most cases. To highlight the reproducibility of the data while preserving the clarity of the figures, we only show duplicate EOB and FB data at pH 7.0. Figure 2 shows that the EOB increases linearly with metal-ion dendrimer loading. At pH 7.0 and 9.0, the G4-NH₂ PAMAM dendrimer can bind up to 220 U(VI) ions without reaching saturation. The uranyl FB is greater than 92% in all cases.

At the present time, we do not have a definitive explanation for this unusually large U(VI) binding capacity of the G4-NH₂ PAMAM dendrimer. However, it could largely be attributed to the high number of uranyl binding sites in the dendrimer. Table 1 shows that the G4-NH₂ PAMAM dendrimer has 64 primary amine (RNH₂) groups, 62 tertiary amine (R₃N) groups and 124 amide (RCONH₂) groups. This corresponds to a total concentration of N and O donors of 5.70×10^{-5} M at pH 7.0 and metal-ion–dendrimer loading of

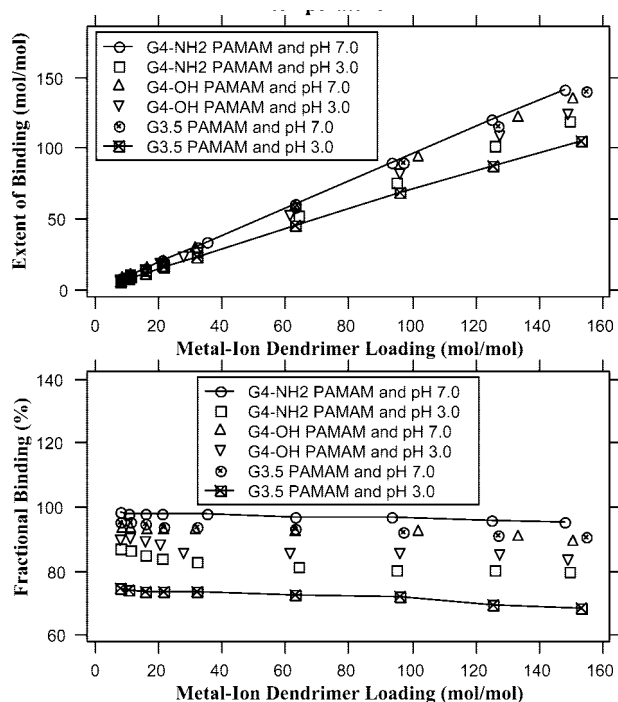


FIGURE 3. Effect of dendrimer terminal group chemistry on the extent of binding and fractional binding of U(VI) in aqueous solutions of PAMAM dendrimers at room temperature.

242. The corresponding uranyl EOB and FB are, respectively, equal to 227 and 94% (Figure 3). The molar ratio of dendrimer N + O donors to UO₂²⁺ ions is ~ 1.54 in this case. Note that water molecules bound to PAMAM dendrimers also provide nonspecific binding sites for metal ions (8, 30). In fact, it is our strong belief that these water molecules play a key role in the ability of PAMAM dendrimers to serve as high capacity chelating agents for metal ions (8, 30, 31). Experimental characterization of water behavior inside a dendrimer and near its surface is very difficult and challenging. For PAMAM dendrimers, Maiti et al. (23) have used molecular dynamics (MD) simulations to estimate the extent of binding (EOB) of water molecules to Gx-NH₂ EDA core PAMAM dendrimers. For G4-NH₂ and G5-NH₂ PAMAM dendrimers, they reported EOB values of 524 and 201 at neutral pH (~ 7.0) (Table 1). Lin et al. (30) also used MD simulations to characterize water penetration within a G5-NH₂ PAMAM dendrimer at high, neutral and low pH. They were able to distinguish between three environmentally defined types of water molecules: (a) water buried inside the dendrimer, (b) water residing at the dendrimer–water interface and (c) bulk water residing outside the dendrimer. Lin et al. (30) were able to estimate the enthalpies and entropies of three classes of water molecules. They found that water molecules located at the surface and inside the G5-NH₂ PAMAM dendrimer have excess free energies of 0.1–0.2 kcal/mol and 0.4–1.3 kcal/mol, respectively. This excess free energy should provide additional driving force for metal ion binding to PAMAM dendrimers in aqueous solutions. Indeed, Ottaviani et al. (31) have estimated that “a portion (about 20%) of Cu(H₂O)₆²⁺ complexes reside in the “water pools” trapped inside earlier generation Gx-NH₂ PAMAM dendrimers ($x < 4$) through quantitative analysis of the ESR spectra of Cu(II) in aqueous solutions of EDA core PAMAM dendrimers. Thus, we anticipate that water molecules bound to PAMAM dendrimers would also coordinate with U(VI) ions as metal ion dendrimer loading increases.

At pH 3.0, Figure 2 also shows significant binding of U(VI) to the G4-NH₂ PAMAM dendrimer (with FB ~ 76 –87% and EOB up to 180) even though its tertiary and primary amine

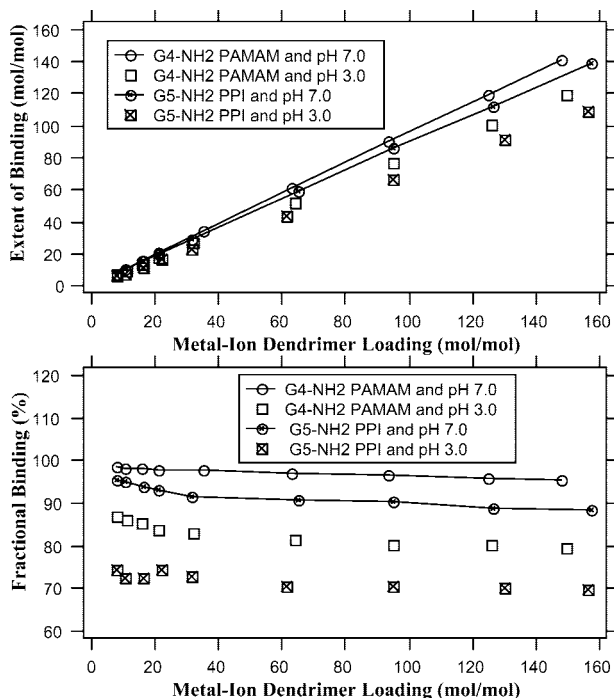


FIGURE 4. Effect of dendrimer branch cell chemistry on the extent of binding and fractional binding of U(VI) in aqueous solutions at room temperature.

groups are fully protonated in this case (SI Table S1). Diallo et al. (8) have measured the EOB and FB of Cu(II) in aqueous solutions of PAMAM dendrimers. They observed no binding of Cu(II) by the dendrimers at pH 5.0 and 3.0. This strongly suggests that uranyl complexation by the G4-NH₂ PAMAM dendrimer at pH 3.0 and 5.0 involves the deprotonation of its amine groups followed by coordination with the UO₂²⁺ metal ion as suggested by Tbal et al. (17). Note that the FB of U(VI) to the G4-NH₂ PAMAM dendrimer at pH 3.0 is slightly lower (by ~5%) than at pH 7.0. We attribute this difference to a slight decrease in the number of available uranyl coordination sites due to the expansion of the fully protonated PAMAM dendrimer in aqueous solutions at pH 3.0. This hypothesis is consistent with recent small angle neutron scattering (SANS) studies of the conformation of a G4-NH₂ PAMAM dendrimer in aqueous solutions by Chen et al. (32). They reported a 4% increase of the dendrimer radius of gyration (R_g) in aqueous solutions at pH ~4.5.

Effects of Terminal Group and Branch Cell Chemistry on U(VI) Binding to Dendrimers. The possibility of attaching functional groups such as primary amines, carboxylates, hydroxyl, etc to dendritic macromolecules is one of the attractive features of dendrimer nanotechnology (7). Core modifications of dendrimers also provide a variety means for controlling critical parameters such as internal and external rigidity, hydrophobicity, void and excluded volumes, and response to stimuli such as changes in solvent polarity and temperature (7). Thus, dendrimer terminal group and core chemistry can be tuned to develop high capacity and selective dendritic ligands that are soluble in appropriate media or bind onto appropriate surfaces. Figure 4 shows the EOB and FB of U(VI) in aqueous solutions of G4-NH₂, G4-OH and G3.5 PAMAM dendrimers. Both the G4-NH₂ and G4-OH PAMAM dendrimers have 62 tertiary amine groups, 124 amide groups and 64 terminal NH₂/OH groups. Conversely, the G3.5 PAMAM dendrimer has 32 tertiary amine groups, 60 amide groups and 64 terminal carboxylic groups. At pH 7.0, we observe significant binding of U(VI) to the G4-OH and G3.5 PAMAM dendrimers. Here again, the EOB increases linearly with metal-ion dendrimer loading without

reaching saturation (Figure 3) due to the large number of dendrimer N and donors. The FB of U(VI) to the G4-NH₂ PAMAM dendrimer varies from 95 to 98%. The FB of uranyl to the G4-OH PAMAM dendrimer is slightly lower (~89–93%) in this case (Figure 3). Note that it is approximately equal to the FB of U(VI) to the G3.5 PAMAM dendrimer (~90–95%) even though this dendrimer has fewer internal amide and amine groups (Table 1).

At pH 3.0, we still observe significant uranyl binding to the G4-OH and G3.5 PAMAM dendrimers. In this case, the FB of U(VI) to the G4-NH₂ PAMAM dendrimer (~80–87%) is comparable to that of the G4-OH PAMAM dendrimer (~83–90%) (Figure 3). Note also that the FB of U(VI) to the G3.5 PAMAM dendrimer (~68–74%) is lower than those of the G4-X PAMAM dendrimers at pH 3.0. The overall results of the measurements suggest that uranyl uptake by PAMAM dendrimers involves the coordination of the metal ion UO₂²⁺ with the amide, tertiary amine, primary amine, and carboxylic groups of the dendrimers. The terminal OH groups of a G4-OH PAMAM do not appear to provide coordination sites for U(VI) ions. This hypothesis is consistent with the recent review of the aqueous coordination chemistry of actinides by Szabó et al. (18). They compared the stability constants ($\log \beta_1$) of aqueous complexes of uranyl with acetate (CH₃COOH) and glycolate (HOCO₂H). They found that the $\log \beta_1$ of the U(VI)–acetate and U(VI)–glycolate complexes are, respectively, equal to 2.44 and 2.16. Because U(VI)–glycolate has a lower stability constant, Szabó et al. (18) concluded that the OH group of the glycolate ligand does not coordinate with U(VI) ions.

Figure 4 compares the EOB and FB of U(VI) in aqueous solutions of a G4-NH₂ PAMAM dendrimer and a G5-NH₂ PPI dendrimer. Both dendrimers have the same number of tertiary and primary amine groups (Table 1). However, propyl chains link the amine groups of PPI dendrimers, whereas those of PAMAM dendrimers are linked by amido(amine) chains. Thus, the G4-NH₂ PAMAM has 64 additional internal amide groups that can coordinate with U(VI) ions (3, 18). Figure 4 highlights the effect of dendrimer branch cell chemistry on uranyl binding. The EOB of U(VI) to the G5-NH₂ PPI dendrimer also increases linearly with metal-ion dendrimer without reaching saturation. Here again, we attribute this behavior to the large number of N and O donors including bound water molecules of the dendrimers (Table 1). At pH 7.0 and molar ratio of U(VI) to dendrimer NH₂ group of 2.4, the FB of uranyl to the PAMAM and PPI dendrimers are, respectively, equal to 95 and 90% (Figure 4). The corresponding EOB are equal to ~140. These results also suggest that uranyl binding to PAMAM and PPI dendrimers in aqueous solutions involves the coordination of the UO₂²⁺ ions with the dendrimer amine groups as reported by Ottaviani et al. (16). At pH 3.0, the FB of U(VI) to the G5-NH₂ PPI dendrimer is still significant (~70–74%). However, it is smaller (by ~10%) than the FB of U(VI) to the G4 PAMAM dendrimer. We attribute this small difference to the amide groups of PAMAM dendrimers, which provide additional coordination sites for U(VI) ions (3, 18).

Effect of Generation on U(VI) Binding to Dendrimers.

A widely held belief in the dendrimer nanotechnology literature is that a gradual transition in overall shape (from a more extended conformation for “earlier” generation dendrimers ($G \leq 3.0$) to a more compact/globular shape for “later” generation dendrimers ($G \geq 5.0$)) causes a significant change in the bulk and solution properties of dendrimers (7). Because of this *dendritic effect*, a dendrimer has (for example) a much smaller intrinsic viscosity than a linear polymer with a similar chemical composition and equal molar mass (7). The characterization of a dendritic effect in coordination chemistry is a major driver of our research program on metal ion chelation by dendrimers (8). Figure

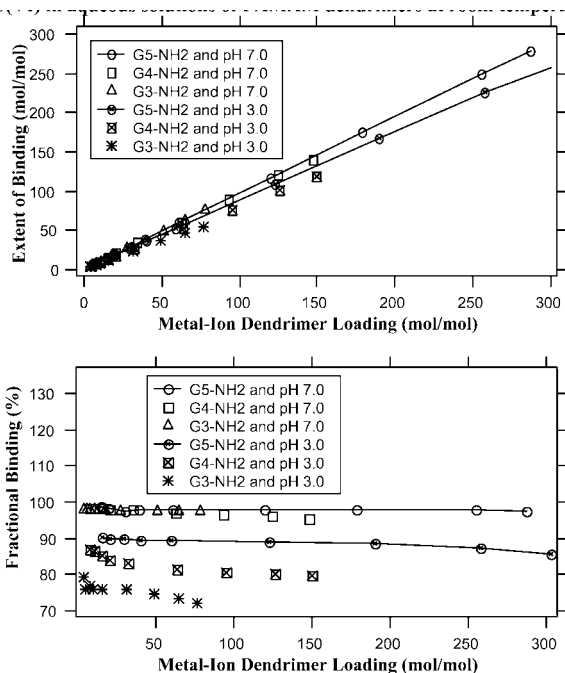


FIGURE 5. Effect of dendrimer generation on the extent of binding and fractional binding of U(VI) in aqueous solutions of PAMAM dendrimers at room temperature.

5 illustrates the effect of dendrimer generation on the EOB and FB of U(VI) in aqueous solutions of G_x-NH₂ PAMAM dendrimers. Here again, the EOB of U(VI) increases linearly with metal-ion dendrimer loading without reaching saturation at pH 7.0 and 3.0 due to the large number of dendrimer N and O donors. Not surprisingly, the higher generation and lower generation dendrimers (G3-NH₂ and G5-NH₂ PAMAM) have, respectively, the highest and lowest uranyl EOB. The larger G5 PAMAM dendrimer has 126 tertiary amine groups, 252 amide group, 128 primary amine groups and 524 bound water molecules at neutral pH (~7.0). This dendrimer can bind 279 uranyl ions without reaching saturation at pH 7.0 and molar ratio of U(VI) to dendrimer NH₂ group of 2.4. Again, we attribute this behavior to the large number of N and O donors including bound water molecules of the dendrimers (Table 1). The corresponding uranyl EOB for the G3 PAMAM dendrimer is ~76. The G3 PAMAM has 30 tertiary amine groups, 32 amide groups and 64 primary amine groups. Note that at pH 7.0, the FB of U(VI) to the G_x-NH₂ PAMAM dendrimers are >95% in all cases. Conversely, the FB of U(VI) to G5-NH₂ PAMAM dendrimer is larger (~85–90%) than that to the G3 PAMAM dendrimer (~71–79%). However, more investigations are warranted before we can attribute the higher uranyl FB of the G5-NH₂ core PAMAM dendrimer at pH 3.0 to a dendritic effect.

Effects of Competing Ligands on U(VI) Binding to Dendrimers. In many cases, liquid effluents from uranium processing facilities contain high concentrations of anions such as NO₃⁻, PO₄³⁻, CO₃²⁻, and Cl⁻ (2–4). Because these inorganic ligands can form a variety of complexes with U(VI) in aqueous solutions (3, 18), it is critical to assess their effects on uranyl binding to dendritic chelating agents. Figure 6 highlights uranyl binding to a G4-NH₂ PAMAM dendrimer in 0.1 and 1.0 M nitric acid (HNO₃) and phosphoric acid (H₃PO₄) solutions. In 0.1 and 1.0 M nitric acid, uranyl ions are present as UO₂(NO₃)₂(H₂O)₂ species (3); whereas UO₂(H₂PO₄)₂ and UO₂(H₂PO₄)⁺ are the predominant uranyl species in 0.1 and 1.0 M phosphoric acid (33). Note that the concentrations of PAMAM dendrimer in the acidic solutions vary from 1.52 × 10⁻⁷ M to 4.63 × 10⁻⁶ M. Thus, they are 5–7 orders of magnitude lower than the concentration

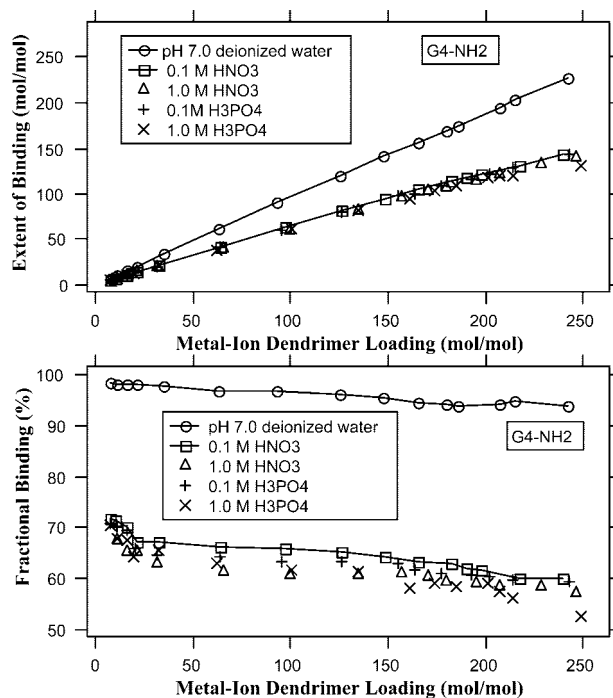


FIGURE 6. Effects of nitric acid (HNO₃) and phosphoric acid (H₃PO₄) on the extent of binding and fractional binding of U(VI) in aqueous solutions of G4-NH₂ PAMAM dendrimer at room temperature.

of the competing NO₃⁻ and PO₄³⁻ ligands. Despite of this, Figure 6 shows significant uranyl binding to the G4 PAMAM dendrimer in 0.1 and 1.0 M nitric and phosphoric acid solutions. At a molar ratio of U(VI) to dendrimer NH₂ group of 3.8, the FB of uranyl to the G4 PAMAM is equal to ~60% in both 0.1 M acid solutions and varies from 52 to 57% in the 1.0 M acid solutions. The corresponding EOB are ~130–144. The fact that both the EOB and FB of U(VI) to the G4 PAMAM dendrimer are comparable in high concentration solutions of competing NO₃⁻ and PO₄³⁻ ligands suggest that uranyl binding to the dendrimers involves coordination of the UO₂²⁺ metal ion with the dendrimer amide and amine groups (3, 18–21).

Figure 7 also shows significant uranyl binding to the G4 PAMAM dendrimer in 0.05 and 0.1 M Na₂CO₃ solutions. At pH ≥ 10.0, (UO₂)(CO₃)₂⁴⁻ is the main uranyl-carbonate species in aqueous solutions and has a large stability constant log K = 21.6 (34). Note that the EOB and FB of U(VI) in the 0.1 M Na₂CO₃ solution are 23–28% larger than those in the 0.1 M HNO₃ and H₃PO₄ solutions even though CO₃²⁻ forms strong complexes with uranyl ions (34). Surprisingly, the FB of U(VI) to the G4 PAMAM dendrimer in the 0.1 M Na₂CO₃ solution is slightly larger than that in the 0.05 M Na₂CO₃ solution. We attribute this higher uranyl binding to an enhanced dendritic macroligand at high pH (~11.0). In this case, all the amine groups of the G4 PAMAM are unprotonated (SI Table S1) and thus available to coordinate with U(VI) ions without overcoming repulsive electrostatic interactions. Figure 7 also shows that the addition of NaCl causes a significant decrease of uranyl binding to the G4 PAMAM dendrimer. At pH 7.0 and 0.1 M NaCl, the FB of uranyl to the G4 PAMAM varies from 50 to 6% (SI Figure S3). We were able to suppress the binding of U(VI) by the G4-NH₂ PAMAM in aqueous solutions containing 1.0 M NaCl at pH 3.0 (Figure 7). Recall that all the amine groups of the G4 PAMAM dendrimer are protonated at pH 3.0 (SI Table S1). Thus, it is not surprising that uranyl binding to this dendrimer is suppressed by the addition of 1.0 M of a hard ligand such Cl⁻ with strong tendency to form ionic bonds with UO₂²⁺

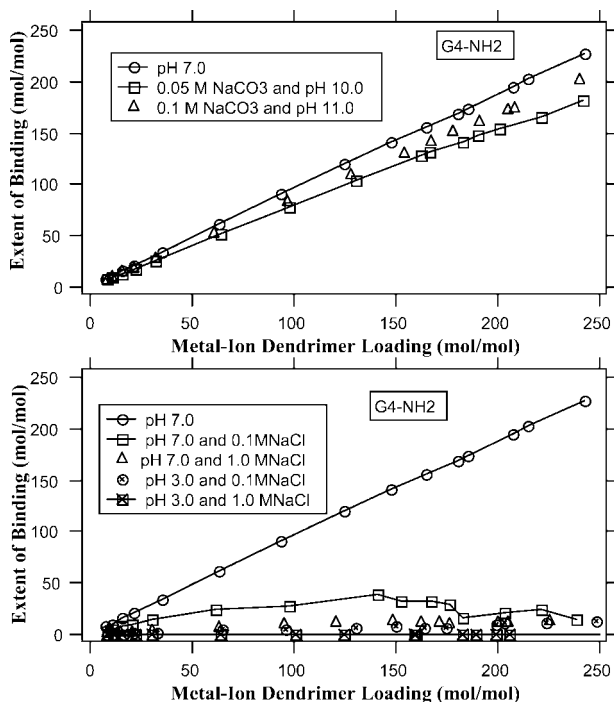


FIGURE 7. Effects of sodium carbonate (Na_2CO_3) and sodium chloride (NaCl) on the extent of binding of U(VI) in aqueous solutions of G4-NH₂ PAMAM dendrimer at room temperature.

metal ions (3). The overall results of this study strongly suggest that dendritic macromolecules such as PAMAM and PPI dendrimers can serve as high capacity and selective chelating ligands for uranyl in aqueous solutions. The unusually large uranyl binding capacity of PAMAM and PPI dendrimers is consistent with our guiding hypothesis that the covalent attachment of O and N donors to flexible chains enclosed within a “soft” and “open” water soluble nanoscale structure generates an enhanced ligand field that acts as “sponge” for metal ions such as U(VI) in aqueous solutions.

Environmental Implications. As previously stated, the mining and processing of uranium ores and the production, reprocessing and disposal of uranium fuel rods generate a broad range of liquid effluents (2–4). The dendrimer enhanced filtration (DEF) (SI Figure S4) developed by Diallo (5, 6) could provide an efficient, cost-effective and environmentally acceptable technology to recover U(VI) from aqueous solutions. The DEF process combines functionalized dendritic nanoparticles with membrane-based separation technologies such as ultrafiltration. This involves the use of dendritic nanoparticles to selectively bind contaminants (e.g., U(VI)) followed by subsequent filtration to produce clean water (SI Figure S4). On a mass basis, the U(VI) binding capacities of the PAMAM and PPI dendrimers are an order of magnitude larger than those of IX resins (28), (33). For example, a G4-NH₂ PAMAM dendrimer can bind up to 227 uranyl ions without reaching saturation (Figure 3). On a mass basis, this is ~4200–4300 mg of U(VI) ions of per g of dendrimer. Note the uranyl binding capacity of typical IX chelating resins with NH₂ groups is ~100 mg/g (33). Because IX is a solid–liquid process, its kinetics is very slow. A contact time of ~24 h between the resin and the liquid is often needed to reach equilibrium (28). A higher concentration (>30 g/L) of salt (NaCl) is also required to strip the bound uranyl [U(VI)] ions from IX resins. Conversely, U(VI) binding to PAMAM dendrimers is very fast and reaches equilibrium in less than 30 min. Note that we were able to suppress the binding of U(VI) by the G4-NH₂ PAMAM in aqueous solutions containing at 0.1 M of sodium chloride at pH 3.0 (Figure 7). This suggests that the bound U(VI) ions can be released in acidic solutions

(pH 3.0) + NaCl (~6 g/L) thereby enabling the recycling of the dendrimers. This also suggests that DEF could be a particularly attractive process for recovering metal ions such as U(VI) from aqueous solutions. Additional experiments are underway to develop low cost alternatives to the expensive PAMAM and PPI dendrimers that were used as model compounds in this study.

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Supporting Information Available

Additional experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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