

# Dendritic Anion Hosts: Perchlorate Uptake by G5-NH<sub>2</sub> Poly(propyleneimine) Dendrimer in Water and Model Electrolyte Solutions

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Perchlorate ( $\text{ClO}_4^-$ ) has emerged as a major groundwater and surface water contaminant in the United States. Ion exchange (IX) is the most widely used technology for treating water containing lower concentrations of perchlorate (<100 ppb). However, a major drawback of IX is the need for frequent regeneration or disposal of the perchlorate-laden resins. As a first step toward the development of high-capacity, selective and recyclable dendritic ligands for the recovery of perchlorate from aqueous solutions by dendrimer filtration, we tested the hypothesis that dendrimers with hydrophobic cavities and positively charged internal groups should selectively bind  $\text{ClO}_4^-$  over more hydrophilic anions such as  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$ . We measured the uptake of  $\text{ClO}_4^-$  by the fifth generation (G5-NH<sub>2</sub>) poly(propyleneimine) (PPI) dendrimer with a diaminobutane core and terminal NH<sub>2</sub> groups in deionized water and model electrolyte solutions as a function of (i) anion–dendrimer loading, (ii) solution pH, (iii) background electrolyte concentration, and (iv) reaction time. The  $\text{ClO}_4^-$  binding capacity of this dendrimer is comparable to those of perchlorate-selective IX resins. However, its  $\text{ClO}_4^-$  binding kinetics is faster and reaches equilibrium in ~1 h. Note also that only a high pH (~9.0) aqueous solution is needed to release more than 90% of the bound  $\text{ClO}_4^-$  anions by deprotonation of the dendrimer tertiary amine groups. The overall results of this study suggest that dendritic macromolecules such as the G5-PPI NH<sub>2</sub> dendrimer provide ideal building blocks for the development of high-capacity, selective and recyclable ligands for the recovery of anions such as perchlorate from aqueous solutions by dendrimer enhanced filtration.

## Introduction

In recent years, perchlorate ( $\text{ClO}_4^-$ ) has emerged as a major groundwater and surface water contaminant in the United States (1–3). Transition metal complexes (4) and nanoscale

zerovalent iron particles (5) are not very effective at reducing perchlorate in aqueous solutions. Although bioreactors can effectively reduce perchlorate to chloride under anaerobic conditions (6), regulatory and public acceptance may limit their utilization in drinking water treatment. Reverse osmosis (RO), nanofiltration (NF), and electro dialysis (ED) are also not cost-effective or efficient at recovering perchlorate from contaminated water in most cases (7). Ion exchange (IX) is the most widely used technology for treating water containing lower concentrations of  $\text{ClO}_4^-$  (<100 ppb) (8–10). However, a major drawback of IX is the need for frequent disposal or regeneration of the perchlorate-laden resins. The dendrimer filtration process developed by Diallo (11–13) could provide a viable alternative to IX for the treatment of water contaminated by anions such as perchlorate once suitable and cost-effective dendritic anions have been identified. As a first step toward the development of high-capacity, selective and recyclable dendritic anion hosts for water treatment, we initially focus on the characterization of perchlorate uptake by dendrimers in water and electrolyte solutions. While significant research efforts have been devoted to the development of selective chelating agents for cation separations (14), anion separations have comparatively received limited attention (15). Unlike cations, anions have filled orbitals and thus do not covalently bind to ligands in most cases. Anions have a variety of geometries (e.g., spherical for  $\text{Cl}^-$  and tetrahedral for  $\text{ClO}_4^-$ ) [Table S1 in the Supporting Information]. Thus, shape-selective receptors may be needed to effectively target anions. The charge-to-radius ratios of anions are also lower than those of cations. Because of this, anion binding to ligands through electrostatic interactions tends to be weaker. Anion binding capacity and selectivity also depend on (i) anion hydrophobicity, (ii) solution pH, and (iii) solvent polarity (15).

Dendritic macromolecules, which include random hyperbranched polymers, dendrigraft polymers, dendrons, and dendrimers are emerging as ideal platforms for the development of advanced materials and processes for water treatment (11–13). Dendrimers consist of three covalently bonded components: a core, interior branch cells, and terminal branch cells. Tomalia and co-workers (16) were among the first investigators to establish that dendrimers can encapsulate anions. They used <sup>13</sup>C NMR spin-relaxation ( $T_1$ ) measurements to show that G4 and G5 poly(amidoamine) (PAMAM) dendrimers with methyl ester terminal groups can encapsulate organic anions such as acetyl salicylic and 2,4-dichlorophenoxyacetic acids in chloroform. Subsequently, Twyman et al. (17) showed that PAMAM dendrimers can bind benzoate. Birnbaum et al. (18) have found that PAMAM dendrimers provide ideal building blocks for the synthesis of ligands for anions such as  $\text{AsO}_4^{3-}$ ,  $\text{CrO}_4^{2-}$ , and  $\text{HPO}_4^{2-}$ . Astruc and co-workers (19) reported the synthesis and characterization of dendrimers with ferrocene groups that can bind  $\text{H}_2\text{PO}_4^-$ ,  $\text{HSO}_4^-$ , and adenosine 5'-triphosphate (ATP) in dichloromethane. Stephan et al. (20) have also described the synthesis of propylene(imine) dendrimers with urea terminal groups that can bind perchlorate and perchlorate in chloroform.

Table S1 shows that  $\text{ClO}_4^-$  has a larger ionic radius and hydration free energy than most anions present in groundwater and surface water. Thus, dendrimers with hydrophobic cavities and positively charged internal groups are expected to selectively bind  $\text{ClO}_4^-$  over more hydrophilic anions such as  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$ . To test this hypothesis, we initially focused on the fifth generation (G5-NH<sub>2</sub>) poly(propylene) (PPI) dendrimer with a diaminobutane (DAB)

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**TABLE 1. Selected Properties of the Dendrimers Evaluated in This Study**

dendrimer	$M_{\text{wth}}^a$	$N_{\text{NT}}^b$	$N_{\text{NH}_2}^c$	$N_{\text{amide}}^d$	$pK_{\text{NT}}^e$	$pK_{\text{NH}_2}^f$	$R_{\text{H}}^g$
G5-NH <sub>2</sub> PPI	7168	62	64	0	6.10	9.75	1.98
G4-NH <sub>2</sub> PAMAM	14215	62	64	64	6.30–6.85	9.23–10.0	2.50

<sup>a</sup>  $M_{\text{wth}}$ : Theoretical molecular weight. <sup>b</sup>  $N_{\text{NT}}$ : Number of tertiary amine groups. <sup>c</sup>  $N_{\text{NH}_2}$ : Number of primary amine groups. <sup>d</sup>  $N_{\text{amide}}$ : Number of amide groups. <sup>e</sup>  $pK_{\text{NT}}$ :  $pK_a$  of dendrimer tertiary amine groups. <sup>f</sup>  $pK_{\text{NH}_2}$ :  $pK_a$  of dendrimer primary amine groups. The  $pK_a$  of the tertiary and primary amine groups ( $pK_{\text{NT}}$  and  $pK_{\text{NH}_2}$ ) of the dendrimers were taken from refs 24 and 25, respectively. <sup>g</sup>  $R_{\text{H}}$ : dendrimer hydrodynamic radius. The  $R_{\text{H}}$  of the G5-NH<sub>2</sub> PPI and G4-NH<sub>2</sub> PAMAM dendrimers are taken from refs 28 and 29, respectively.

**TABLE 2. Extents of Protonation of the Dendrimers Evaluated in This Study<sup>a</sup>**

G5-NH <sub>2</sub> PPI	pH 4.0	pH 7.0	pH 9.0	pH 11.0
$\alpha_{\text{NT}}$	0.99	0.11	0.00	0.00
$\alpha_{\text{NH}_2}$	0.99	0.99	0.81	0.00

G4-NH <sub>2</sub> PAMAM	pH 4.0	pH 7.0	pH 9.0	pH 11.0
$\alpha_{\text{NT}}$	0.99	0.17–0.41	0.00	0.00
$\alpha_{\text{NH}_2}$	0.99	0.99	0.63–0.91	0.02–0.09

<sup>a</sup> The extents of protonation of the tertiary and primary amine groups ( $\alpha_{\text{NT}}$  and  $\alpha_{\text{NH}_2}$ ) of the PPI and PAMAM dendrimers were calculated using the Henderson-Hasselbach equation (24, 25):  $\log \alpha'/1 - \alpha' = pK_a' - \text{pH}$ ; where  $i = \text{NT}$  and  $\text{NH}_2$ .

core and terminal NH<sub>2</sub> groups (Figure S1 of Supporting Information). This is a water-soluble dendrimer with 64 terminal NH<sub>2</sub> groups and 62 internal tertiary amine groups (Table 1) that can encapsulate hydrophobic organic compounds such as Rose Bengal and pyrene (21–23). In this study, we measured the uptake of perchlorate by a G5-NH<sub>2</sub> PPI dendrimer in deionized water and electrolyte solutions. The model electrolyte solutions consisted of mixtures of deionized water + monovalent and divalent anions including Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. Selected measurements of perchlorate uptake were also carried out in (i) aqueous solutions of a G4-NH<sub>2</sub> PAMAM dendrimer with ethylene diamine core (Figure S1) and (ii) mixtures of G5-PPI and G4-NH<sub>2</sub> PAMAM dendrimers with monovalent and divalent anions. The G4-NH<sub>2</sub> PAMAM dendrimer has 64 terminal NH<sub>2</sub> groups, 64 internal amide groups, and 62 internal tertiary amine groups (Table 1). The overall results of these experiments suggest that dendritic macromolecules such as the G5-PPI NH<sub>2</sub> dendrimer provide ideal building blocks for the development of high-capacity, selective and recyclable ligands for the recovery of perchlorate from aqueous solutions by dendrimer filtration (11–13).

## Experimental Section

**Materials.** Reagent-grade sodium perchlorate (NaClO<sub>4</sub>), sodium chloride (NaCl), sodium nitrate (NaNO<sub>3</sub>), sodium bicarbonate (NaHCO<sub>3</sub>), and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) from Sigma-Aldrich were used, respectively, as sources of ClO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. G5-NH<sub>2</sub> PPI and G4-NH<sub>2</sub> PAMAM dendrimers in methanol solutions were purchased from Sigma-Aldrich and used as received. Table 1 gives selected properties of the PPI and PAMAM dendrimers evaluated in this study. The  $pK_a$  of the dendrimer tertiary and primary amine groups ( $pK_{\text{NT}}$  and  $pK_{\text{NH}_2}$ ) were taken from refs 24 and 25, respectively. Their extents of protonation (Table 2) were calculated using the Henderson–Hasselbach equation (24–25). Diallo et al. (25) have shown that this simplified methodology gives results comparable in accuracy to those obtained using theoretically derived dendrimer protonation models (26–27). The hydrodynamic radii ( $R_{\text{H}}$ ) of the G5-NH<sub>2</sub> PPI and G4-NH<sub>2</sub> PAMAM dendrimers were taken from refs 28 and 29, respectively.

**Methods and Procedures.** Batch experiments were carried out in deionized water and model electrolyte solutions to measure the extent of binding (EOB) of ClO<sub>4</sub><sup>-</sup> as a function of (i) anion–dendrimer loading, (ii) solution pH, and (iii) reaction time using the procedures described by Diallo et al. (25). The binding assay procedure consisted of (i) mixing and equilibrating aqueous solutions of ClO<sub>4</sub><sup>-</sup> + dendrimer at room temperature, (ii) separating the perchlorate–dendrimer solutions from the aqueous solutions by ultra-filtration (UF), and (iii) measuring the ClO<sub>4</sub><sup>-</sup> concentrations of the initial solutions and filtrates. Diallo et al. (25) have found that the pH of dendrimer complexes can be controlled (within 0.1–0.2 pH unit) by addition of concentrated acid (e.g., HNO<sub>3</sub>) or base (e.g., NaOH). The concentrations of perchlorate in the solutions [ClO<sub>4</sub><sup>-</sup>]<sub>o</sub> and filtrates [ClO<sub>4</sub><sup>-</sup>]<sub>f</sub> were measured using a Dionex DX120 ion chromatograph with conductivity suppression and detection (3). The ClO<sub>4</sub><sup>-</sup> detection limit was ~4 ppb. The concentration of bound perchlorate [ClO<sub>4</sub><sup>-</sup>]<sub>b</sub> (mol/L) was expressed as

$$[\text{ClO}_4^-]_{\text{b}} = [\text{ClO}_4^-]_{\text{o}} - [\text{ClO}_4^-]_{\text{f}} \quad (1)$$

The EOB (moles of bound perchlorate per mole of dendrimer), the concentration of dendrimer [ $C_{\text{d}}$ ] (mol/L) in solution and the fractional binding [FB] (%) were expressed as

$$\text{EOB} = \frac{[\text{ClO}_4^-]_{\text{b}}}{C_{\text{d}}} \quad (2)$$

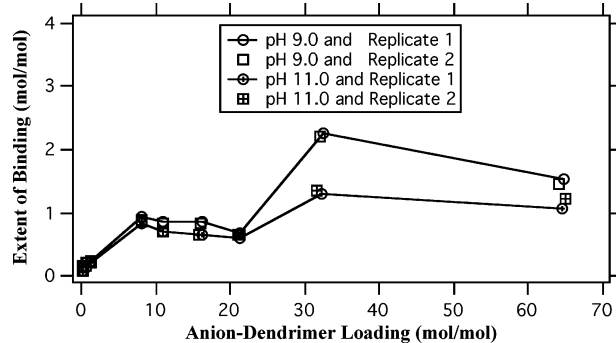
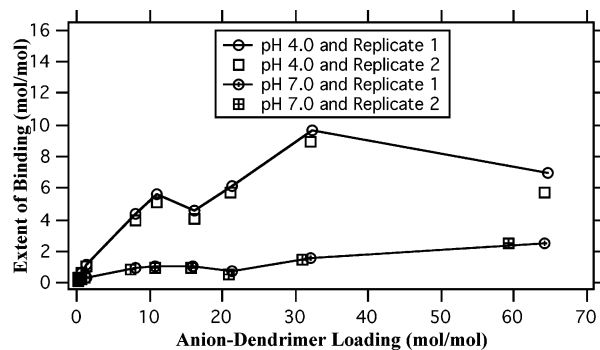
$$C_{\text{d}} = \frac{m_{\text{d}}}{V_{\text{s}}M_{\text{wd}}} \quad (3)$$

$$\text{FB} = 100 \times \frac{[\text{ClO}_4^-]_{\text{b}}}{[\text{ClO}_4^-]_{\text{o}}} \quad (4)$$

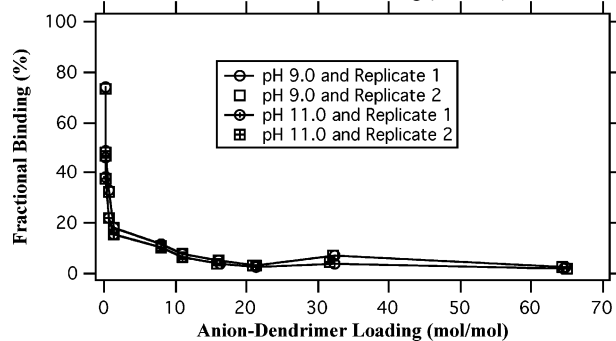
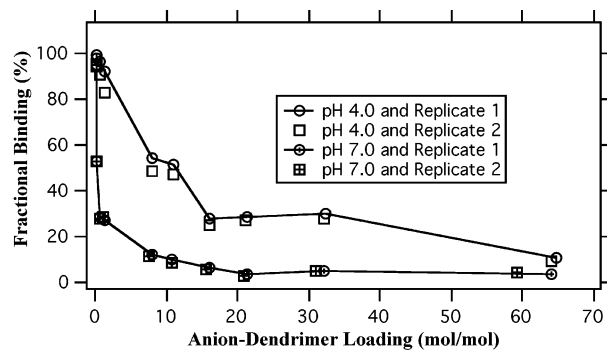
where  $m_{\text{d}}$  (g) is the mass of dendrimer in solution,  $V_{\text{s}}$  (L) is the solution volume, and  $M_{\text{wd}}$  (g/mol) is the dendrimer molar mass (Table 2).

## Results and Discussion

Figures 1 and 2 show the effects of anion–dendrimer loading and solution pH on the EOB and FB of ClO<sub>4</sub><sup>-</sup> to a G5-NH<sub>2</sub> PPI dendrimer in deionized water at room temperature and reaction time of 1 h. In these experiments, we varied the molar ratio of perchlorate to dendrimer to prepare solutions with a given anion–dendrimer loading. Three replicate measurements were carried out in each set of experiments. To highlight the reproducibility of the data while preserving the clarity of the figures, we only plot duplicate measurements. Figure 1 shows that the EOB of perchlorate goes through a series of distinct binding steps at pH 4.0 as anion–dendrimer loading increases. First, we observe a gradual increase of the EOB to a maximum of ~6.0 mol of bound ClO<sub>4</sub><sup>-</sup> per mol of dendrimer when the anion–dendrimer loading is ~11.0. This is followed by another increase of the EOB [~9.0 for an anion–dendrimer loading of ~32.0] and a slight decrease to a value of ~7.0 when the anion–dendrimer



**FIGURE 1.** Extent of binding of perchlorate to G5-NH<sub>2</sub> PPI dendrimer in deionized water at room temperature and reaction time of 1 h. The initial perchlorate concentration in solution is 1000 ppb (0.01 mM).



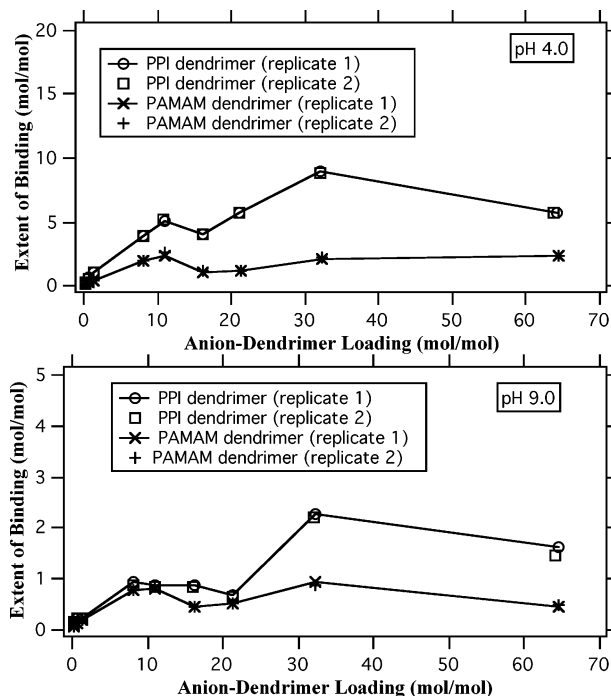
**FIGURE 2.** Fractional binding of perchlorate to G5-NH<sub>2</sub> PPI dendrimer in deionized water at room temperature and reaction time of 1 h. The initial perchlorate concentration in solution is 1000 ppb (0.01 mM).

loading is ~64.0. The FB of perchlorate also exhibits a series of distinct binding steps in aqueous solutions of the G5-NH<sub>2</sub> PPI dendrimer (Figure 2). At pH 4.0 and low anion-dendrimer loading (~0.17–1.29), the FB is greater than 90% in all cases. Note that the FB sharply decreases and levels off around 30% followed by a slight decrease as anion-dendrimer loading increases. Because each successive perchlorate binding step involves an initial increase of solute binding

followed by a second increase (Figures 1 and 2), we attribute this behavior to the presence of dendrimer “sites” with different binding capacity and affinity for ClO<sub>4</sub><sup>-</sup>. As the sites near the dendrimer surface become filled, the ClO<sub>4</sub><sup>-</sup> guests diffuse inside the dendritic host to occupy its internal and confined cavities. This mode of guest uptake by a macromolecular host is commonly referred to as topological trapping in the supramolecular chemistry literature (21). Note that a dendrimer often undergoes conformational rearrangements as it accommodates guest molecules (21). Thus, the slight decrease of the EOB of ClO<sub>4</sub><sup>-</sup> to a value of ~7.0 when the anion-dendrimer loading is ~64.0 could be attributed to the release of “loosely” bound guests as the G5-NH<sub>2</sub> PPI dendrimer rearranges itself to provide a favorable environment for perchlorate anions.

Two potential driving forces for perchlorate uptake by the G5-NH<sub>2</sub> PPI dendrimer are (i) electrostatic interactions between ClO<sub>4</sub><sup>-</sup> anions and protonated amine groups of the dendrimer and (ii) hydrophobic partitioning in the dendrimer interior. Figure 2 illustrates the role of the electrostatic interactions between ClO<sub>4</sub><sup>-</sup> and the dendrimer protonated tertiary amine groups as a key driving force of perchlorate uptake. At pH 4.0, 99% of the dendrimer tertiary amine groups are protonated (Table 2). As shown in Figure 2, 98% of ClO<sub>4</sub><sup>-</sup> are bound to the dendrimer at pH 4.0 when the anion-dendrimer loading is ~0.31. Conversely, the FB of ClO<sub>4</sub><sup>-</sup> in aqueous solutions of the G5-NH<sub>2</sub> PPI dendrimer is ~53% at pH 7.0 and anion-dendrimer loading of 0.31. In this case, only 11% of the tertiary amine groups of the dendrimer are protonated; whereas 99% of its primary amine groups remain protonated (Table 2). Note that the maximum EOB of ClO<sub>4</sub><sup>-</sup> (~2.5 at anion-dendrimer loading of 32.0) decreases by a factor of 4 at pH 7.0 compared to that at pH 4.0. The maximum EOB of ClO<sub>4</sub><sup>-</sup> (~2.20) is also smaller at pH 9.0 and anion-dendrimer loading of 32.0 (Figure 1) even though ~81% of the dendrimer NH<sub>2</sub> groups remain protonated (Table 2). This suggests that electrostatic interactions between ClO<sub>4</sub><sup>-</sup> and protonated NH<sub>2</sub> groups of the dendrimer do not have a significant effect on perchlorate uptake. Figure 1 also shows some binding of ClO<sub>4</sub><sup>-</sup> [with a maximum EOB ~1.29 at anion-dendrimer loading of 32.0] at pH 11.0 when both the tertiary and primary amines of the G5-NH<sub>2</sub> PPI dendrimer are unprotonated (Table 2). We attribute this “residual” binding to the topological trapping of ClO<sub>4</sub><sup>-</sup> anions inside the hydrophobic cavities of the PPI dendrimer. This hypothesis is consistent with the results of fluorescence spectroscopic studies of pyrene binding to a G5-NH<sub>2</sub> PPI dendrimer in aqueous solutions carried out by Pistolis and Malliaris (23). They reported that polarity of the interior of a G5-NH<sub>2</sub> PPI dendrimer is comparable to that of hexane; which has a dielectric constant  $\epsilon_{\text{hexane}} = 2.0$  (23). Thus, a hydrophobic guest such as pyrene is “pushed deeper and deeper inside the dendrimer” where it becomes shielded from the water phase (23).

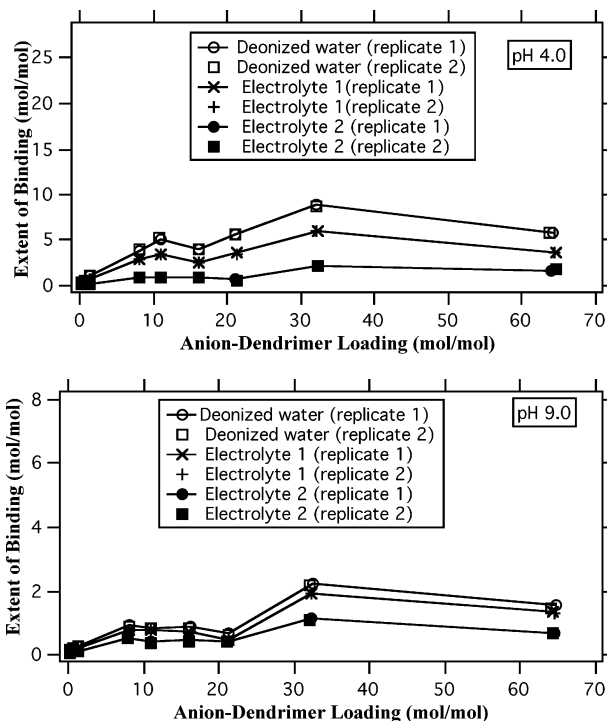
To test the hypothesis that the G5-NH<sub>2</sub> PPI dendrimer provides a more favorable environment for the partitioning of ClO<sub>4</sub><sup>-</sup> anions than the more hydrophilic PAMAM dendrimers, we measured perchlorate uptake in aqueous solutions of a G4-NH<sub>2</sub> PAMAM dendrimer at pH 4.0 and 9.0. This dendrimer has the same number of tertiary amine and primary groups as the G5-NH<sub>2</sub> PPI dendrimer (Table 1). The extents of protonation of the tertiary and primary amine groups of the PPI and PAMAM dendrimers are comparable (Table 2). However, the G4-NH<sub>2</sub> PAMAM dendrimer is more hydrophilic. Indeed, it has 64 additional internal amide groups that can interact with water through hydrogen bonding. Molecular dynamics simulations of Gx-NH<sub>2</sub> PAMAM dendrimers with explicit water molecules carried out by Goddard and co-workers (30) showed extensive water penetration in the interior of a G4-NH<sub>2</sub> PAMAM dendrimer.



**FIGURE 3.** Extent of binding of perchlorate to G5-NH<sub>2</sub> PPI and G4-NH<sub>2</sub> PAMAM dendrimers in deionized water at room temperature and reaction time of 1 h. The initial perchlorate concentration in solution is 1000 ppb (0.01 mM).

Niu et al. (27) reported an estimated value of  $\epsilon_{\text{dendrimer}} = 23$  for the internal dielectric constant of a G4-NH<sub>2</sub> PAMAM dendrimer thereby suggesting that its polarity is similar to that of ethanol, which has a dielectric constant  $\epsilon_{\text{ethanol}} = 24$  (31). Figure 3 shows the EOB of perchlorate to the G4-NH<sub>2</sub> PAMAM dendrimer in deionized water. The corresponding FB curve (Figure S2) is given in the Supporting Information. In this case, the EOB curve also goes through a series of distinct binding steps at pH 4.0 with a maximum EOB  $\sim 2.3$ . This value is smaller (by a factor of 4.5) than the EOB of ClO<sub>4</sub><sup>-</sup> to the PPI dendrimer in deionized water even though the tertiary amine groups of the PAMAM dendrimer are fully protonated at pH 4.0 (Table 2). Similarly, at pH 9.0, the maximum EOB of ClO<sub>4</sub><sup>-</sup> ( $\sim 0.9$ ) in aqueous solutions of the PAMAM dendrimer is also smaller (by a factor of  $\sim 2.4$ ). These results are consistent with our hypothesis that the hydrophobic G5-NH<sub>2</sub> PPI dendrimer provides a more favorable environment for ClO<sub>4</sub><sup>-</sup> than the more hydrophilic G4-NH<sub>2</sub> PAMAM dendrimer.

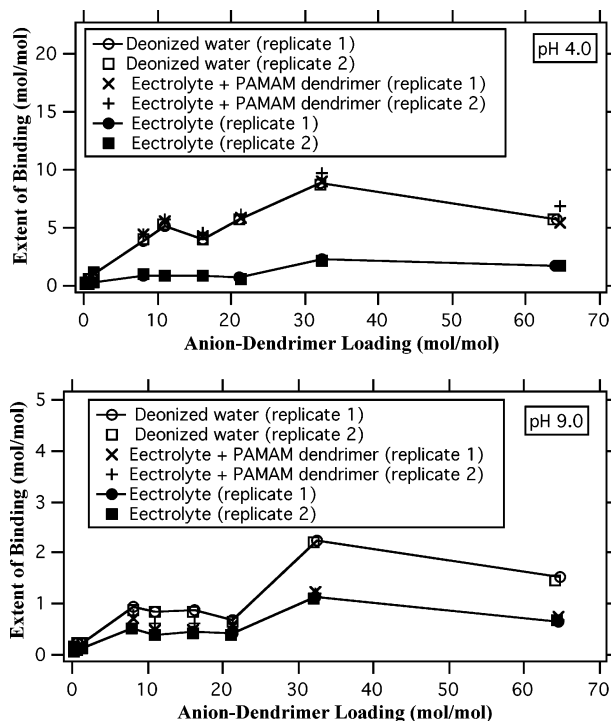
To assess the effects of competing anions on perchlorate uptake by the G5-NH<sub>2</sub> PPI dendrimer, we measured the EOB of ClO<sub>4</sub><sup>-</sup> in two model electrolyte solutions at pH 4.0 and 9.0 (Figure 4). The low background electrolyte (Electrolyte 1) consisted of a solution of 0.1 mM NaCl, 0.3 mM NaHCO<sub>3</sub>, 0.1 mM NaNO<sub>3</sub>, and 0.1 mM Na<sub>2</sub>SO<sub>4</sub> with an initial molar ratio of SO<sub>4</sub><sup>2-</sup> to ClO<sub>4</sub><sup>-</sup> equal to 10.0. The high background electrolyte (Electrolyte 2) was similar to that used by Gu et al. (8) in their recent study of ClO<sub>4</sub><sup>-</sup> and U(VI) sorption onto IX resins with quaternary alkyl ammonium groups. It consisted of a solution of 1.0 mM NaCl, 3.0 mM NaHCO<sub>3</sub>, 1.0 mM NaNO<sub>3</sub>, and 1.0 mM Na<sub>2</sub>SO<sub>4</sub> with an initial molar ratio of SO<sub>4</sub><sup>2-</sup> to ClO<sub>4</sub><sup>-</sup> equal to 100.0. Figure 4 compares the uptake of perchlorate by the G5-NH<sub>2</sub> PPI dendrimer in deionized water and electrolytes. The corresponding FB curve (Figure S3) is given in the Supporting Information. In the low background electrolyte solution, the maximum EOB ( $\sim 6.0$ ) decreases by a factor of 1.5 compared to that observed in deionized water ( $\sim 9.0$ ) at pH 4.0. Note that perchlorate uptake by the G5-NH<sub>2</sub> PPI dendrimer is still appreciable even though



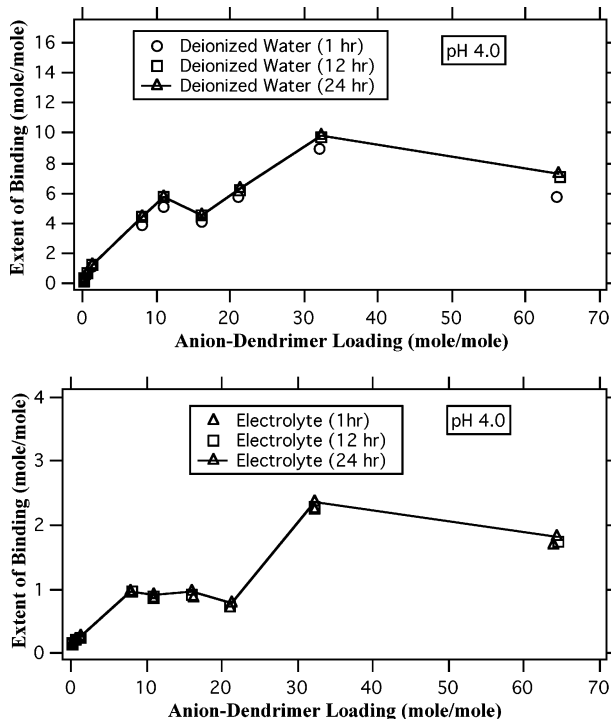
**FIGURE 4.** Extent of binding of perchlorate to G5-NH<sub>2</sub> PPI dendrimer in deionized water and model electrolyte solutions at room temperature and reaction time of 1 h. The initial perchlorate concentration in solution is 1000 ppb (0.01 mM). Electrolyte 1 consists of an aqueous solution containing 0.1 mM NaCl, 0.3 mM NaHCO<sub>3</sub>, 0.1 mM NaNO<sub>3</sub>, and 0.1 mM Na<sub>2</sub>SO<sub>4</sub>. Electrolyte 2 consists of an aqueous solution containing 1.0 mM NaCl, 3.0 mM NaHCO<sub>3</sub>, 1.0 mM NaNO<sub>3</sub>, and 1.0 mM Na<sub>2</sub>SO<sub>4</sub>.

the molar concentration of the divalent SO<sub>4</sub><sup>2-</sup> anions in solution is 10 times higher than that of the ClO<sub>4</sub><sup>-</sup> anions. At pH 4.0, Figure 4 shows a large decrease of the maximum EOB of perchlorate ( $\sim 2.0$ ) in the high background electrolyte solution compared to that observed in deionized water ( $\sim 9.0$ ) at anion-dendrimer loading of  $\sim 32.0$ . At pH 9.0, the maximum EOB of perchlorate in deionized water ( $\sim 2.20$ ) is comparable to that in the low background electrolyte solution ( $\sim 1.95$ ). However, it is  $\sim 1.78$  times larger than the measured EOB of perchlorate ( $\sim 1.10$ ) in the high background electrolyte solution. Recall that the initial molar ratio of SO<sub>4</sub><sup>2-</sup> to ClO<sub>4</sub><sup>-</sup> in the high background electrolyte solution is equal to 100. Thus, the presence of “excess” amounts of SO<sub>4</sub><sup>2-</sup> anions in solution has a significant impact on perchlorate uptake by the G5-NH<sub>2</sub> PPI dendrimer.

The preferential removal of divalent anions (e.g., SO<sub>4</sub><sup>2-</sup>) over monovalent anions (e.g., ClO<sub>4</sub><sup>-</sup>) has been observed in IX resins with quaternary alkyl ammonium groups (8–9, 32). Barron and Fritz (32) coined the term “electroselectivity” to explain the preference for divalent anions over monovalent ions in these systems. We carried out measurements of ClO<sub>4</sub><sup>-</sup> uptake by a mixture of G5-PPI and G4-NH<sub>2</sub> PAMAM dendrimers in the high background electrolyte solution to gain insight into SO<sub>4</sub><sup>2-</sup> electroselectivity in aqueous solutions of dendrimers + anions. A key objective of these experiments was to “suppress” sulfate electroselectivity by addition of a hydrophilic dendrimer with protonated amine groups. Indeed, we expect the hydrophilic G4-NH<sub>2</sub> PAMAM dendrimer to provide a more favorable environment for SO<sub>4</sub><sup>2-</sup> than the more hydrophobic G5-NH<sub>2</sub> PPI dendrimer. To test this hypothesis, we varied the molar ratio of SO<sub>4</sub><sup>2-</sup> to PAMAM dendrimer to prepare solutions with sulfate-dendrimer loadings equal to those of perchlorate-dendrimer loadings used in previous experiments (Figures 1, 3, and 4). For the



**FIGURE 5.** Extent of binding of perchlorate to G5-NH<sub>2</sub> PPI dendrimer in deionized water, electrolyte, and mixture of electrolyte + G4-NH<sub>2</sub> PAMAM dendrimer at room temperature and reaction time of 1 h. The initial perchlorate concentration in solution is 1000 ppb (0.01 mM). The electrolyte consists of an aqueous solution containing 1.0 mM NaCl, 3.0 mM NaHCO<sub>3</sub>, 1.0 mM NaNO<sub>3</sub>, and 1.0 mM Na<sub>2</sub>SO<sub>4</sub>.



**FIGURE 6.** Extent of binding of perchlorate to G5-NH<sub>2</sub> PPI dendrimer in deionized water and electrolyte at room temperature as a function of reaction time. The initial perchlorate concentration in solution is 1000 ppb (0.01 mM). The electrolyte consists of an aqueous solution containing 1.0 mM NaCl, 3.0 mM NaHCO<sub>3</sub>, 1.0 mM NaNO<sub>3</sub>, and 1.0 mM Na<sub>2</sub>SO<sub>4</sub>.

G5-NH<sub>2</sub> PPI dendrimer, the molar ratios of ClO<sub>4</sub><sup>-</sup> to dendrimer were also equal to those in previous experiments (Figures 1, 3, and 4). Figure 5 shows that addition of the G4-NH<sub>2</sub> PAMAM

dendrimer in the high background electrolyte solution “suppresses” the effect of SO<sub>4</sub><sup>2-</sup> on perchlorate uptake by the G5-NH<sub>2</sub> PPI dendrimer. Note that the EOB and FB of ClO<sub>4</sub><sup>-</sup> in deionized water (Figure 5 and Figure S4 of Supporting Information) are equal to those in the high background electrolyte solution when the G4-NH<sub>2</sub> PAMAM dendrimer is added to the solution. Conversely, the addition of the PAMAM dendrimer has no effect on perchlorate uptake in the high background electrolyte solution (Figures 5 and S4) at pH 9.0 when the tertiary amine groups of the G4-NH<sub>2</sub> PAMAM dendrimer are neutral (Table 2). In this case, the EOB and FB of ClO<sub>4</sub><sup>-</sup> in the mixtures of the PPI and PAMAM dendrimers are lower than those in deionized water. Note they are equal to the EOB and FB of ClO<sub>4</sub><sup>-</sup> in the high background electrolyte solution. This suggests that the suppression of the effect of sulfate on perchlorate uptake by the PPI dendrimer in the high background electrolyte solution involves SO<sub>4</sub><sup>2-</sup> binding to the protonated tertiary amine groups of the G4-NH<sub>2</sub> PAMAM dendrimer. These results also provide indirect evidence that (i) the G5-NH<sub>2</sub> PPI dendrimer selectively binds ClO<sub>4</sub><sup>-</sup> over more hydrophilic anions such as Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and HCO<sub>3</sub><sup>-</sup>, and (ii) the SO<sub>4</sub><sup>2-</sup> anions bound to the G4-PAMAM dendrimer can be released by deprotonation of its tertiary amine groups. However, more direct measurements are needed to further corroborate these indirect observations. Finally, we would like to point out that perchlorate uptake by the G5-NH<sub>2</sub> PPI dendrimer in aqueous solutions reaches equilibrium in ~1 h (Figure 6 and Figure S5 of Supporting Information).

### Environmental Implications

As stated in the Introduction, ion exchange (IX) is the most widely used process for treating water contaminated by lower concentration of ClO<sub>4</sub><sup>-</sup> (<100 ppb) (8–10). Two commonly used IX resins for perchlorate removal are (i) nonselective resins and (ii) selective resins. Resin regeneration/reuse and brine management/disposal are two critical issues that have a major impact on the efficiency, cost effectiveness, and environmental acceptability of IX systems used to treat water contaminated by ClO<sub>4</sub><sup>-</sup>. The nonselective resins require frequent regenerations with brine (~6–12 wt % NaCl solution) due to their low ClO<sub>4</sub><sup>-</sup> sorption capacity/selectivity (9). This generates wastes (brine + ClO<sub>4</sub><sup>-</sup>) that need to be pretreated prior to disposal (9). Conversely, the ClO<sub>4</sub><sup>-</sup> selective resins do not require frequent regenerations. However, even concentrated brine solutions (~12 wt %) are not effective at regenerating the resins in most cases because of their strong binding affinity for ClO<sub>4</sub><sup>-</sup>. Because of this, spent ClO<sub>4</sub><sup>-</sup> selective resins are incinerated in most cases following a single use. Although Gu et al. (9) have shown that a solution of 1.0 M FeCl<sub>3</sub> + 4.0 M HCl could regenerate ClO<sub>4</sub><sup>-</sup> selective resins, the treatment of the regenerant solutions involves the use of a flow-through reactor operating at high temperature (190–204 °C) to reduce perchlorate using concentrated solutions of ferrous iron and/or nontoxic organic reducing agents. Dendrimer filtration (11–13) could provide a viable alternative to IX for the treatment of ClO<sub>4</sub><sup>-</sup> contaminated water once suitable dendritic ligands have been identified. This process combines functionalized dendritic nanomaterials with membrane-based separation technologies such as ultrafiltration (UF). The G5-NH<sub>2</sub> PPI dendrimer (Figure S1) has a molar mass of 7168 Da and a hydrodynamic radius (*R*<sub>h</sub>) of 1.98 nm (21–22). Thus, it can be effectively separated from aqueous solutions by UF (11). As shown in Figure 1, the maximum EOB of ClO<sub>4</sub><sup>-</sup> in aqueous solutions at pH 4.0 is ~9.0 for an anion-dendrimer loading of ~32.0. On a mass basis, this corresponds to a binding capacity of 125 mg of ClO<sub>4</sub><sup>-</sup> per g of dendrimer. Gu et al. (9) have measured the sorption of ClO<sub>4</sub><sup>-</sup> onto nonselective and selective IX in aqueous solutions and model electrolytes at

pH 8.5. They obtained sorption capacity <1.0 mg/g for a nonselective resin with trimethyl ammonium groups (Purolite A850). Conversely, they reported  $\text{ClO}_4^-$  sorption capacity of 75 mg/g for a selective bifunctional polystyrene resin with ethyl/hexyl ammonium groups. In both cases, the equilibrium concentration of  $\text{ClO}_4^-$  in water is equal to 200 ppb. Thus, the  $\text{ClO}_4^-$  binding capacity of the G5-NH<sub>2</sub> PPI dendrimer is comparable to those of selective IX resins with trialkyl ammonium groups that have been evaluated by Gu et al. (9).

The presence of competing divalent anions such as  $\text{SO}_4^{2-}$  can greatly limit the efficiency and longevity of IX resins used to recover perchlorate from contaminated water (8, 9). Figure 4 shows that  $\text{SO}_4^{2-}$  anions can greatly reduce the perchlorate binding capacity of the G5-NH<sub>2</sub> PPI dendrimer in electrolyte solutions. However, the addition of a more hydrophilic dendrimer such as a G4-NH<sub>2</sub> PAMAM dendrimer can “suppress” the effect of  $\text{SO}_4^{2-}$  anions on the  $\text{ClO}_4^-$  binding capacity and selectivity of the G5-NH<sub>2</sub> PPI dendrimer in electrolytes (Figure 6). This suggests that mixtures of dendrimers can be used to effectively recover perchlorate from aqueous solutions containing high concentrations of divalent anions such as  $\text{SO}_4^{2-}$  (32). Because perchlorate uptake by the G5-NH<sub>2</sub> PPI dendrimer occurs in a homogeneous liquid–liquid process, its kinetics is relatively fast and reaches equilibrium in ~1 h (Figure 7). Conversely, IX is a heterogeneous solid–liquid process that involves ion diffusion through the resin pores followed by an exchange reaction. Not surprisingly,  $\text{ClO}_4^-$  binding to the IX resins requires at least 24 h before it reaches equilibrium in most cases (8, 9). Finally, we would like to point out the significant decrease of the EOB and FB  $\text{ClO}_4^-$  in aqueous solutions of the G5-NH<sub>2</sub> PPI dendrimer at pH 9.0 and 11.0. Note that most perchlorate-selective IX resins contain sites that can be exchanged with  $\text{ClO}_4^-$  at any pH. Thus, they cannot be regenerated by a simple change of solution pH. Conversely, only a high pH (~10–11.0) aqueous solution will be needed to release more than 90% to the G5-NH<sub>2</sub> PPI dendrimer by deprotonation of its tertiary amine groups. The overall results of this study suggest that dendritic macromolecules such as the G5-NH<sub>2</sub> PPI dendrimer provide ideal building blocks for the development of high-capacity, selective and recyclable ligands for perchlorate. Additional experiments and computer-aided molecular design studies are underway to develop high-capacity, selective and recyclable dendritic anion hosts (33) for recovery of anions such as  $\text{ClO}_4^-$  from aqueous solutions by dendrimer filtration (11–13).

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## Supporting Information Available

Table S-1 and Figures S-1–S-5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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