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Synergistic Effects of Combinations of Cationic Polyaminoamide Dendrimers/Anionic Polyelectrolytes on Amorphous Silica Formation: A Bioinspired Approach

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This paper reports the inhibition efficiency of combinations of amine-terminated polyaminoamide (PAMAM) dendrimers of generation 1 and 2 and anionic polyelectrolytes in colloidal silica particle growth. The polyelectrolytes studied were PAA = polyacrylate (low MW is 2 KDa, high MW is 450 KDa), PAM-*co*-AA = poly(acrylamide-*co*-acrylate) of MW 200 KDa, CMI = carboxymethylinulin (proprietary MW, between 2 and 3 KDa). The principle findings are summarized as follows: (1) PAMAM-1 and -2 dendrimers are effective inhibitors of silica growth at 40 ppm dosage levels. (2) The effect of anionic polycarboxylates on the inhibitory activity of PAMAM-1 and PAMAM-2 is dosage-dependent. They do not affect PAMAM-1 inhibitory activity; they increase that of PAMAM-2 at low dosage (20 ppm) but exhibit detrimental effects at high dosage (>40 ppm), with CMI exerting no adverse effects at any dosage. (3) Negative charge density on the polymer is directly proportional to inhibitor activity deterioration. (4) Addition of polymer prevents dendrimer entrapment into the silica colloidal matrix by preventing formation of SiO_2−dendrimer precipitates. This research was inspired by the recognition that diatom biosilica-associated peptides (silaffins natSil-1 and natSil-2) and long-chain polyamines (LCPA) profoundly influence silica formation from a silicic acid solution in vitro.

Introduction

Formation of amorphous hydrated silica (biosilica) in living organisms and higher plants is an important process frequently referred to as “biosilicification”.[1] Among biogenic minerals, of which carbonates (e.g., calcium carbonate) and phosphates (e.g., hydroxyapatite) are the most prevalent, silica appears to be unique in many respects. Whereas widespread carbonate and phosphate salts are crystalline ionic solids whose precipitation is governed by solubility equilibria, silica is an amorphous oxide formed by a complicated inorganic polymerization process, leading to a variety of morphological patterns and structures.[2] It is well-established that organic biomolecules are involved in biosilica formation and these have mainly been studied in sponges and diatoms.[2] Insight into the nature of this organic matrix has been realized through characterization of diatom biosilica-associated peptides (silaffins natSil-1 and natSil-2) and long-chain polyamines (LCPA), both of which accelerate silica formation from a silicic acid solution in vitro.[3] Furthermore, it has been suggested that formation of organic matrices composed of polyanionic natSil-2-like phosphoproteins and polycationic silica-forming components may represent a widespread mechanism in diatom biosilica morphogenesis.[4]

Nanopatterned silica formation may be a precisely chosen pathway in nature that leads to preferred structural motifs; however, this is not the case in several engineering applications, such as in water chemical technology. In supersaturated silica-laden process waters, silicate ion polymerizes via a condensation polymerization mechanism, at appropriate pH regions.[5] The resulting amorphous silica precipitate, after Ostwald ripening,[6] is transformed into a hard and tenacious scale deposit on critical industrial equipment, such as heat exchangers, transfer pipes, etc. Silica removal by dissolution is a challenge,[7] thus limiting the usual control approaches to maintaining undersaturation (leading to water wastage) or pretreatment (with high capital/equipment costs). Biochemical studies have shown that polycationic macromolecules (either alone or in combination with anionic biopolymers) profoundly influence in vivo silica formation.[1−4]

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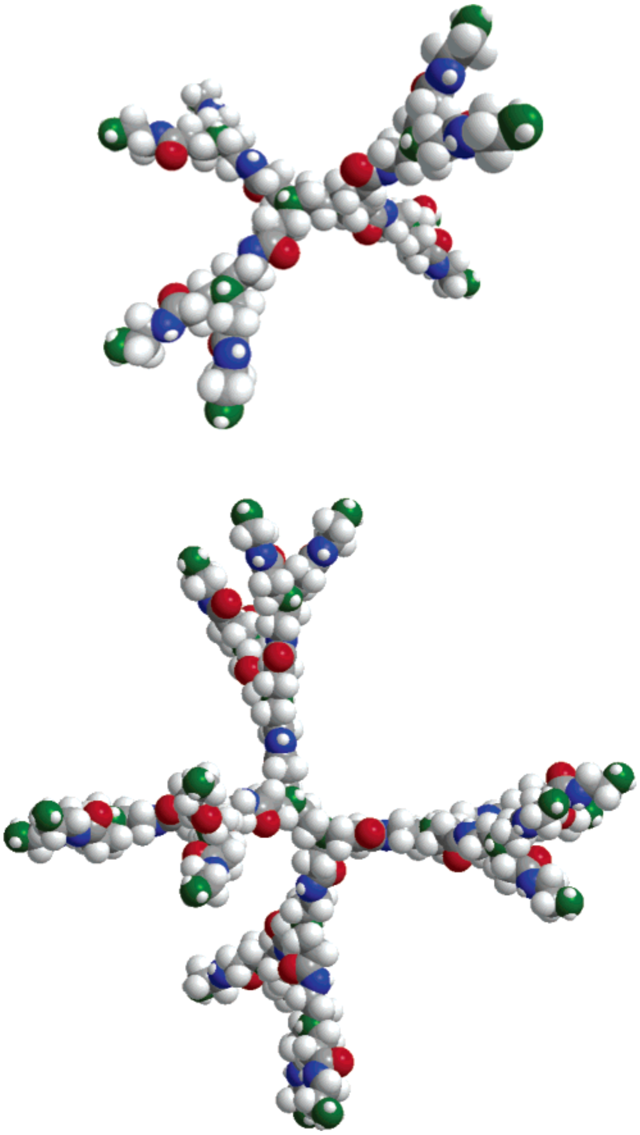

Figure 1. Energy-minimized space-filling models of PAMAM-1 (upper, 6 internal and 8 surface amine groups, 2.2 nm hydrodynamic diameter) and PAMAM-2 (lower, 14 internal and 16 surface amine groups, 2.9 nm hydrodynamic diameter). Color codes: green, internal and surface amine groups; blue, amide nitrogen atoms; red, amide and carboxylate oxygen atoms; gray, carbon atoms; off-white, hydrogen atoms.

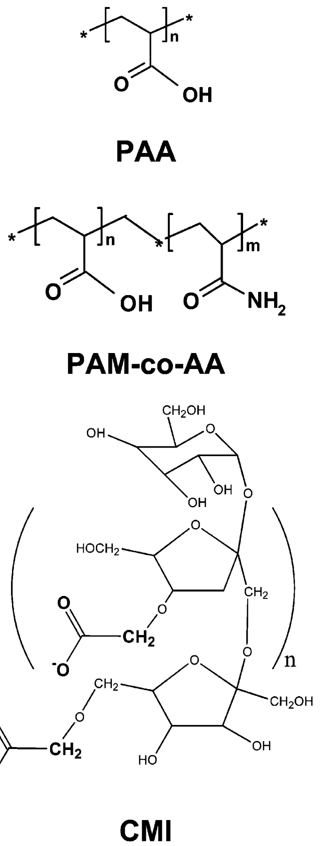

Figure 2. Schematic structures of PAA, PAM-*co*-AA ($n = 80$, $m = 20$ w/w), and CMI.

Researchers at the interface of chemistry and biology have, since long ago, been utilizing each other's knowledge and expertise, not only to get deeper insight into complex biochemical processes involved in natural systems but also to design novel materials inspired by nature.[1−4]

Our ongoing studies focus on the inhibitory effects of polycationic molecules on colloidal silica formation by studying the solubility enhancement of silicate ions. We have selected to utilize polyaminoamide (PAMAM) dendrimers,[8] Figure 1, for these reasons: (a) they are available in anionic (HOOC-terminated) or cationic (H_2N-terminated) forms, (b) they are available in various generations (as generation number increases, dendrimer size and branching both increase), (c) they possess precise topological features (in contrast to several cationic polymers that possess ill-defined structural features and molecular weights and are often polydisperse). The research described herein is part of our broader research efforts that are focused on developing new approaches for scale growth control, as it relates to chemical treatment of process waters.[9]

Experimental Section

Instruments. IR spectra were recorded on a FT−IR Perkin−Elmer FT 1760. The measurements of soluble silicate made with a HACH 890 spectrophotometer from the Hach Co., Loveland, CO.

Reagents and Chemicals. Sodium silicate $Na_2SiO_3{\cdot}5H_2O$ was from EM Science (Merck). PAMAM dendrimers were from Aldrich Chemical Co. (Milwaukee, WI) as 20% w/v solutions in methanol. PAMAMs are available under the commercial name STARBURST polymers.

The anionic polyelectrolytes studied (see Figure 2) were PAA, polyacrylate (low MW is 2 KDa from Polysciences, Inc., high MW is 450 KDa, from Aldrich Chemical Co.); PAM-*co*-AA, poly(acrylamide-*co*-acrylate) of MW 200 KDa, 20 wt % acrylamide (from Aldrich Chemical Co.); and CMI, carboxymethylinulin (proprietary MW, between 2 and 3 KDa, from Solutia Inc.). Ammonium molybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) and oxalic acid ($H_2C_2O_4{\cdot}2H_2O$) were from EM Science (Merck). Sodium hydroxide

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(NaOH) was from Merck, hydrochloric acid 37% was from Riedel de Haen. Potassium bromide (KBr) for preparation of the IR discs was from Fluka. Acrodisc filters (0.45 μ) were from the Pall−Gelman Corporation. In-house, nanopure water was used for all experiments. This water was tested for soluble silica and was found to contain negligible amounts.

Preparation of Supersaturated Silicate Solutions. A solution containing silicate, 500 ppm as SiO_2, was prepared by dissolving 4.4 g of $Na_2SiO_3{\cdot}5H_2O$ in 2.5 L of nanopure water. Stock solutions of the additives in water were 1% (10 000 ppm). The following solutions were prepared for the silicate spectrophotometric detection test: (a) 10 g of ammonium molybdate were dissolved in 100 mL of water, and its pH was adjusted to between 7 and 8 with NaOH to avoid precipitation of ammonium molybdate; (b) HCl 1 + 1 was prepared by mixing one volume of 37% HCl with an equal volume of water; (c) 8.75 g of oxalic acid was dissolved in 100 mL of water. All solutions were kept in PET containers (glass containers must be avoided to minimize SiO_2 dissolution and silicate leaching into the test solutions).

Silicate Polymerization Protocol. *Control Test.* One-hundred milliliters from the 500 ppm silicate stock solution was placed in a PET beaker that contained a Teflon-covered magnetic stir bar. The pH of this solution was initially ~11.8 and was adjusted to 7.00 ± 0.1 by the addition of HCl and NaOH (the change in the resulting volume was about 3%). The beaker was then covered with plastic membrane and set aside without stirring. The solutions were checked for the soluble silica by the silicomolybdate method every 2 h for the first 12 h or at 24, 48, and 72 h time intervals after the pH reduction.

Inhibitor Test. One-hundred milliliter portions of the 500 ppm SiO_2 stock solution were placed in PET containers charged with Teflon-covered magnetic stir bars. In each container, different volumes of inhibitor (10 000 ppm stock solution) were added to achieve the desirable inhibitor concentration. These ranged from 20 to 40, 60, and 80 ppm, and the volumes where added were 200, 400, 600, and 800 μL. After that, the same procedure as that used for the control test was followed.

Determination of Soluble (Reactive) Silica. Frequently, there is a misconception on the use of the terms "silica" and "silicate". For example, in several publications, the term "soluble silica" actually refers to "soluble silicate", and the two terms are frequently used (incorrectly) interchangeably. In this paper, the term silica indicates the product of silicate polymerization. The term "silicate" indicates all the forms of the species $Si(OH)_4$ at various deprotonated states. Soluble silicate was measured using the silicomolybdate spectrophotometric method. According to this method, a 2 mL filtered sample from the test solution, with a 0.45 μm syringe filter, is diluted to 25 mL in the cell, with a light path of 1 cm. One millilter of ammonium molybdate stock solution and 0.5 mL of 1 + 1 HCl are added to the sample cell; the solution is mixed well and left undisturbed for 10 min. One millilter of oxalic acid solution is then added, and the solution is mixed again. The solution is set aside for 2 min. After the second time period, the photometer is set at zero absorbance with water. Finally, the sample absorbance is measured at 452 nm as "parts per million of soluble silicate". The detectable concentration range is 0−75.0 ppm. To calculate the concentration in the original solution, a dilution factor is applied.

The silicomolybdate method is based on the principle that ammonium molybdate reacts only with "reactive" silicate and any phosphate present at low pH (about 1.2) and yields heteropoly acids that are yellow in color. Oxalic acid is added to destroy the molybdophosphoric acid, leaving silicomolybdate intact and eliminating any color interference from phosphates. It should be emphasized that molybdate reacts only with soluble silicate forms, but is totally unreactive to colloidal silica species. This was verified experimentally in our laboratory.

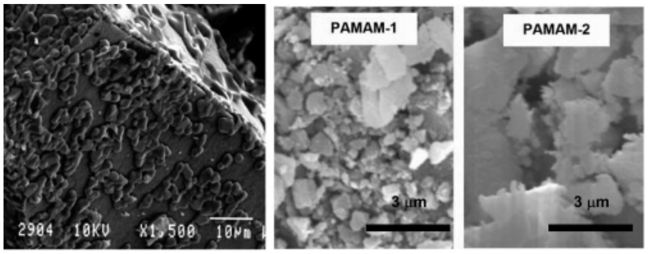

Figure 3. Morphology of colloidal silica precipitates in the absence (left) and presence of PAMAM-1 (center) and PAMAM-2 (right).

Results

Various generations of PAMAM dendrimers were screened by a well-established silicate supersaturation test.[10] Aqueous solutions of 500 ppm silicate (from sodium silicate, expressed as SiO_2) were utilized herein.[11] Under conditions of high silicate supersaturation, carboxylate-terminated dendrimers (PAMAM-0.5, PAMAM-1.5, and PAMAM-2.5, deprotonated at pH 7.0) exhibited low efficacy for silicate polymerization inhibition. In contrast, amine-terminated dendrimers (PAMAM-1 and PAMAM-2, protonated at pH 7.0) exhibited excellent inhibitory activity.[9b] This dramatic difference is undoubtedly due to the cationic nature of the latter. The exact inhibitory mechanism largely remains unexplored, but the dendrimers' interference with the polymerization pathway and subsequent stabilization of soluble silicates (monomers, dimers, trimers, etc.) is a fact. However, because of the dendrimers' inability to achieve complete inhibition, the resulting colloidal silica particles appear as insoluble precipitates. There are two competing pathways occurring concurrently: silicate polymerization inhibition and colloidal silica aggregation into larger colloids. These SiO_2−dendrimer precipitates were collected and studied by elemental analysis, XRD, FT−IR, and SEM.[12] They are amorphous (XRD powder patterns[12]) and are composed of silica and entrapped dendrimer (elemental analyses and FT−IR spectra[13]). The presence of either PAMAM-1 or PAMAM-2 has profound effects on particle morphology.

PAMAM-1, a more effective silica inhibitor than PAMAM-2, results in silica particles that are singificantly reduced in size (~0.5 μm, center image in Figure 3) compared to silica precipitates without any additives (~50 μm, left image in Figure 3) and those with PAMAM-2 present (>6 μm, right image in Figure 3). An additional feature of the silica precipitates in the presence of either PAMAM-1 or PAMAM-2 is that they appear more irregular in shape compared to uninhibited silica. Last, silica particles in the presence of PAMAM-1 exhibit a lower tendency to aggregate compared to those in the presence of PAMAM-2. This is

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(11) These are considered to be "high-stress" conditions with respect to silicate supersaturation, but necessary for differentiation between inhibitor efficiencies. Most untreated industrial process waters operate at <200 ppm SiO_2.

(12) See the Supporting Information.

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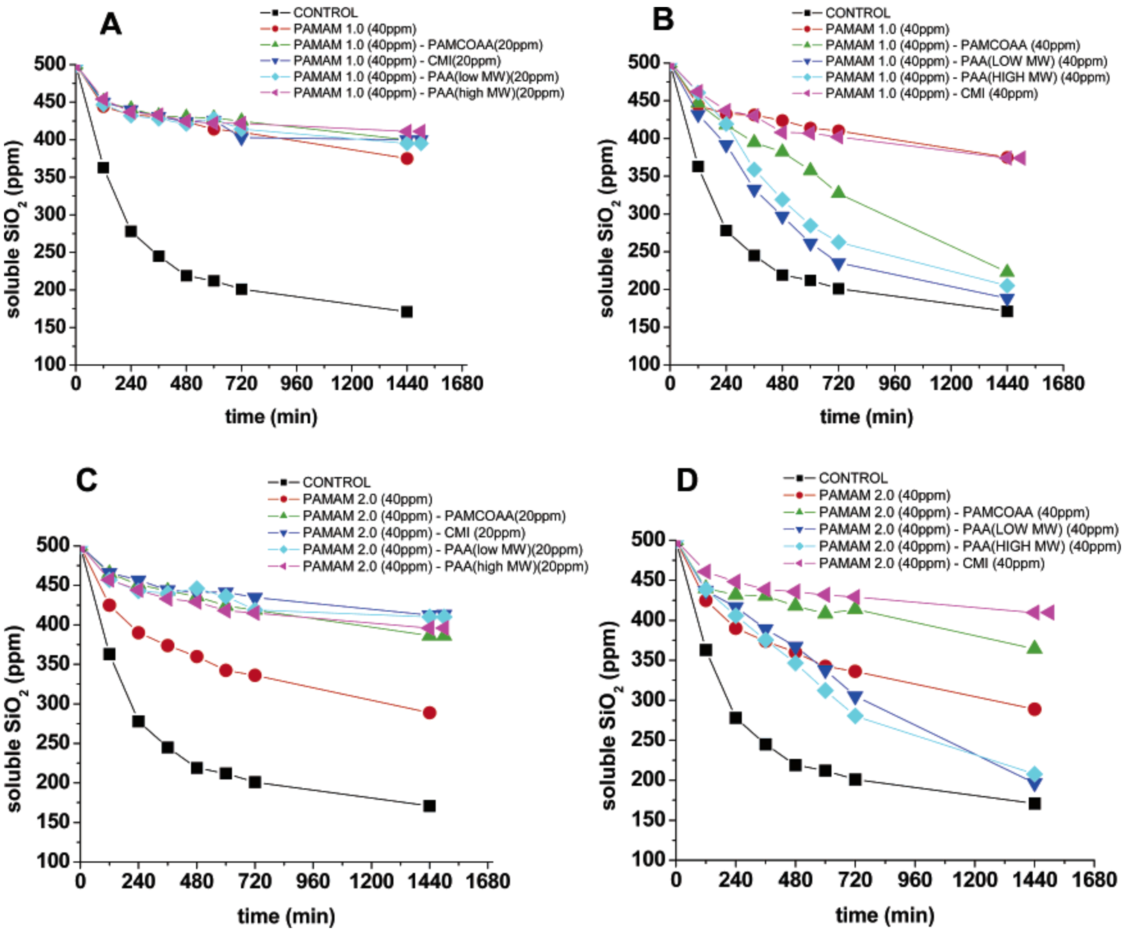

Figure 4. Inhibition of silicate polymerization by PAMAM-1 (A and B) and PAMAM-2 (C and D) in combination with various anionic polyelectrolytes.

consistent with the larger size and higher branching of PAMAM-2 (compared to PAMAM-1), which can more effectively act as a bridge between silica particles.

Dendrimer entrapment within the silica matrix is responsible for inhibitor depletion from solution, leading to deterioration of inhibitory activity. This problem can be alleviated by the addition of anionic polyelectrolytes in silicate solutions containing PAMAM-1 or 2 designed to “neutralize” some of the dendrimer cationic charge. This “bioinspired approach” originates from the premise that anionic polyelectolytes may play a controlling role on the effect of polycations on biosilica. These are polyacrylate (PAA, low MW 2 KDa, high MW 450 KDa), poly(acrylamide-*co*-acrylate) (PAM-*co*-AA, MW 200 KDa), and carboxymethylinulin (CMI, proprietary MW, 2−3 KDa), and their choice was made on the basis of the following: (a) potential for application as additives in process waters; (b) they all contain the same functional groups (−COOH); (c) there is a systematic anionic charge “dilution” from PAA to PAM-*co*-AA and CMI, with the number of bonds separating the charge on the $-COO^-$ being 6, 8, and 14, respectively.

The time-dependent inhibition plots (Figure 4) reveal significant observations that point to a dendrimer-polymer “synergism”. Addition of carboxylate-containing polymers at a 20 ppm dosage in solutions containing PAMAM-1 (at 40 ppm) has no effect on soluble silicate levels (Figure 4A); however, they inhibit the formation of SiO_2−dendrimer precipitates (vide supra). However, a polymer dosage increase to 40 ppm causes a substantial drop in soluble silicate, with PAA showing the most notable decrease (Figure 4B), but still higher than the control (235 ppm for low MW PAA and 263 ppm for high MW PAA compared to 201 ppm for the control after 8 h). PAM-*co*-AA at 40 ppm dosage causes a decrease of PAMAM-1 inhibitory activity (loss of ∼100 ppm soluble silicate, but ∼125 ppm higher than the control). CMI added at either 20 or 40 ppm dosage does not affect inhibitory activity of PAMAM-1.

Combinations of PAMAM-2 (40 ppm) and any of the anionic polymers (20 ppm) cause a dramatic increase in inhibitory activity (from ∼60 to ∼84%), Figure 4C. However, a dosage increase of the polymer to 40 ppm results in substantial differentiation in inhibition (Figure 4D). In the presence of PAA (either low or high MW), soluble silicate levels follow essentially values comparable to those with PAMAM-2 alone within the first 8 h, but drop further (to ∼300 ppm, 60%). In solutions containing combinations of PAMAM-2 (40 ppm) and either PAM-*co*-AA or CMI (40 ppm), soluble silicate levels remain unaffected and are comparable to those with a 20 ppm CMI dosage. A further polymer dosage increase to 60 ppm appears to have detrimental effects on inhibitory activity (data not shown here).[12] Combinations of PAMAM-1 (40 ppm) and PAM-*co*-AA (60 ppm) stabilize silicate at 380 ppm after 8 h (160 ppm more than the control and ∼40 ppm less than with PAMAM-1 alone). A blend of PAMAM-1 (40 ppm) and

Table 1. Inhibition of Silicate Polymerization Data by PAMAM-1 and 2 in Combination of Anionic Polymers

additive(s)	dendrimer/polymer molecular ratio	soluble silicate (ppm)[a]	soluble silicate ($M \times 10^{-3}$)	silicate/dendrimer molecular ratio	estimated silicate/dendrimer molecular ratio[b]	inhibitor efficiency[c]
PAMAM-1 (40 ppm)		202	4.58	164	30	5.45
PAMAM-1 (40 ppm) + PAM-*co*-AA (20 ppm)	280	217	4.92	176	30	5.86
PAMAM-1 (40 ppm) + PAA-low (20 ppm)	2.8	206	4.67	167	30	5.56
PAMAM-1 (40 ppm) + PAA-high (20 ppm)	631	214	4.85	173	30	5.78
PAMAM-1 (40 ppm) + CMI (20 ppm)	3.5	201	4.56	163	30	5.43
PAMAM-1 (40 ppm) + PAM-*co*-AA (40 ppm)	140	115	2.61	93	30	3.10
PAMAM-1 (40 ppm) + PAA-low (40 ppm)	1.4	27	0.61	22	30	0.73
PAMAM-1 (40 ppm) + PAA-high (40 ppm)	∼315	55	1.25	45	30	1.48
PAMAM-1 (40 ppm) + CMI (40 ppm)	∼1.8	200	4.54	162	30	5.40
PAMAM-2 (40 ppm)		128	2.90	236	62	3.81
PAMAM-2 (40 ppm) + PAM-*co*-AA (20 ppm)	123	211	4.79	389	62	6.28
PAMAM-2 (40 ppm) + PAA-low (20 ppm)	1.23	211	4.79	389	62	6.28
PAMAM-2 (40 ppm) + PAA-high (20 ppm)	277	207	4.69	382	62	6.16
PAMAM-2 (40 ppm) + CMI (20 ppm)	1.54	227	5.15	419	62	6.75
PAMAM-2 (40 ppm) + PAM-*co*-AA (40 ppm)	∼62	206	4.67	380	62	6.13
PAMAM-2 (40 ppm) + PAA-low (40 ppm)	∼0.6	97	2.20	179	62	2.88
PAMAM-2 (40 ppm) + PAA-high (40 ppm)	∼138	73	1.66	135	62	2.17
PAMAM-2 (40 ppm) + CMI (40 ppm)	∼0.8	221	5.01	408	62	6.57

[a] These numbers indicate soluble silicate (in parts per million) at 720 min after subtraction of soluble silicate without additives (208 ppm). [b] The estimation of the predicted silicate/dendrimer molecular ratio was based on the hypothesis that one N−H group stabilizes one silicate molecule. For PAMAM-1, 30 such moieties were calculated (14 internal, 24 peripheral) and for PAMAM-2, 62 such moieties were calculated (14 internal and 48 peripheral). [c] Defined as the number of silicate molecules stabilized as found experimentally divided by the estimated silicate molecules stabilized per molecule of dendrimer.

CMI (60 ppm) shows virtually unaffected inhibitory activity (∼400 ppm silicate stabilization after 8 h). A dosage increase of PAM-*co*-AA or CMI to 60 ppm has no further detrimental effect, and the inhibition plots are reminiscent of those for 20 ppm (Figure 4B) or 40 ppm dosages (Figure 4D). It is important to note that silica precipitates do not form in the presence of combinations of PAMAM-1 or PAMAM-2 with the aforementioned polyanions. Instead, slightly turbid dispersions are obtained that are stable for several months. This visual effect presents corroborative evidence that the addition of anionic polyelectrolytes not only enhances soluble silicate levels but also “alleviates” silica precipitate formation and subsequent inhibitor entrappment into the amorphous silica matrix.

Discussion

An analysis of the above results was sought in order to correlate molecular structure and number of amine functional groups involved in inhibitory activity. This approach is presented in detail in Table 1. There are a number of facts and hypotheses taken into account for this: (a) All anionic polyelectrolytes do not exhibit any inhibitory activity at the dosages of 20 and 40 ppm, as verified experimentally. (b) The dendrimer amine groups (actually in their protonated form at the experimental pH) are involved in inhibition. This is supported by the fact that carboxylate-terminated PAMAM dendrimers (generations 0.5, 1.5 and 2.5) show only marginal inhibitory activity.[10] (c) Each $-NH^+$ group (internal groups) stabilizes one silicate molecule and each $-NH_3^+$ (peripheral groups) stabilize three silicate molecules, pressumably via hydrogen-bonding interactions. This estimation leads to 164 silicate molecules stabilized per one molecule of PAMAM-1 and 236 molecules of silicate per molecule of PAMAM-2. (d) The amide groups ($-C(O)-NH-$) do not contribute to inhibitory activity. (e) Internal voids within the dendrimer structure are able to stabilize monosilicates and other oligosilicates. These are all considered soluble silicates, as they are reactive to the silicomolybdate test.

Careful examination of the data presented in Table 1 shows that PAMAM-1 alone (in the absence of anionic polymeric additives) stabilizes 5.45 times more silicates compared to the predicted number. In the same context, PAMAM-2 stabilizes 3.81 times more silicates than what is predicted by the aforementioned analysis. This difference in inhibitory activity between PAMAM-1 and 2 relates undoubtedly to the number of amine groups available by each dendrimer. Inhibitory activity cannot directly be related to the number of amine groups. If that were the case, PAMAM-2 should show higher inhibition performance than PAMAM-1, which is not the case. It has been reported in the literature that positively charged, protonated amine groups accelerate silica formation and also act as colloidal silica aggregators toward formation of larger colloids.[16,17] Polymeric structure has been found to affect the resulting silica morphological features in an unpredictable manner, leading to nanopatterns or to amorphous solids. Presence of either PAMAM-1 or -2, albeit efficient inhibitors, also results in the formation of silica colloids. The presence of silica precipitates (with dendrimer entrapped in it) originates from the portion of silicate that is not inhibited.

Inhibition of silica growth is insufficiently understood. It should be emphasized that silicate polymerization inhibition and colloidal silica stabilization are two completely different approaches. The latter aims at maintaining small silica

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(15) Carboxyl-terminated PAMAMs (generations 0.5, 1.5, 2.5) exist as zwitter ions at pH ∼7 because of internal tertiary amine groups ($\equiv NH+$) and show marginal inhibitory activity at high concentrations ($>$100 ppm). It is reasonable to assume that silicate enters the internal dendrimer voids and becomes “shielded” from the polymerization reaction.

colloids dispersed (in suspension) and at avoidance of deposition. In contrast, the former delays (ideally ceases) silicate polymerization, thus maintaining silicate in its soluble forms. Colloidal silica ideally does not form in that case. This approach is sought in this research. The inhibitor “disrupts” condensation polymerization of silicate by interfering with nucleophilic attack of neighboring silicate ions (an S_N2-like mechanism).

Amine-terminated PAMAMs associate with silicate ions or small silica oligomers, thus preventing further growth. As mentioned above, the silica supersaturations achieved in the presence of PAMAM-1 and -2 (Table 1) support the conclusion that silicate stabilization is not a stoichiometric phenomenon. This leads to the hypothesis that stabilized larger (oligo)silicates must be present either within the dendrimer voids or at the periphery. Unfortunately, the silicomolybdate test cannot distinguish between various forms of silicates.

Carboxyl-terminated PAMAM’s (generations 0.5, 1.5, and 2.5, at least partially deprotonated at test pH) apparently cannot function similarly, because the negative charge from the carboxylate groups is dominant. It is well-established that anionic small molecules and polymers do not inhibit silicate polymerization.[9b] All dendrimers possess “internal” amide functionalities that may play a role in enhancing silicate solubility.

The presence of anionic polyelectrolytes affects inhibition performance of the dendrimers. This effect depends on a number of variables: (a) polymer dosage, (b) polymer structure, (c) anionic charge density. Combinations of PAMAM-1 and all polymers (at 20 ppm dosage) exhibit unaltered inhibition efficiency compared to PAMAM-1 alone. However, an increase in polymer dosage to 40 ppm has a profound effect on PAMAM-1 behavior. Figure 4B clearly shows that the PAA polymers with the highest anionic charge density substantially reduce PAMAM-1’s inhibition performance by neutralizing some of the cationic charge needed for inhibition. PAM-*co*-AA, on the other hand, with lower charge density than PAA, exhibits a lesser inhibition reduction effect on PAMAM-1. CMI with the lowest charge density has virtually no detrimetal effects on PAMAM-1. Supersaturated silicate containing both PAMAM-1 and CMI present no turbidity. This is an indication of absence of large silica colloids. This observation seems consistent with the polymers actually acting as inhibitors of the dendrimer’s propensity to aggregate silica colloids toward flocculation and formation of larger silica particles.

Combination of the anionic polymers (20 ppm dosage) with PAMAM-2 actually improves the latter’s performance (Figure 4C and Table 1). Because these polyanions do not inherently contribute to silica formation inhibition, the only explanation for this performance enhancement is that they associate with PAMAM-2 (pressunably through polyanion−polycation ionic interactions) and thus inhibit the dendrimer’s propensity for colloidal silica aggregation. However, if the anionic polymer dosage is increased to 40 ppm, effective cation−anion charge neutralization does not allow the amine groups to be involved in inhibition. Again, anionic charge density has an effect on PAMAM-2 that is similar to its effect on PAMAM-1 (Figure 4D).

Growth of crystalline inorganic salts is controlled by use of anionic “small molecules” (commonly phosphonate inhibitors)[18] or polyacrylate polymers and derivatives.[19] Mineral-scale inhibitors achieve inhibition by stereospecific adsorption onto crystallographic planes of a growing nucleus and thus “poison” further growth.[20] These mechanisms are not applicable for silica inhibition because of its amorphous nature.

Conclusions

The purpose of this work is to delineate the effect of cationic dendrimer−anionic macromolecule combinations on silica formation. The principle findings are summarized as follows: (1) PAMAM-1 and -2 dendrimers are effective inhibitors of silica growth at 40 ppm dosage levels. (2) The effect of anionic polycarboxylates on the inhibitory activity of PAMAM-1 and -2 is dosage-dependent. They do not affect PAMAM-1 inhibitory activity, but increase that of PAMAM-2 at low dosage (20 ppm) and exhibit detrimental effects at high dosage ($>$40 ppm). CMI exerts no adverse effects at any dosage. (3) Negative charge density on the added polymer is directly proportional to inhibitor activity deterioration. (4) Addition of polymer prevents dendrimer entrapment into the silica colloidal matrix by preventing formation of SiO_2−dendrimer precipitates.

Elegant work by Clarson and Perry[16] and Wright[17] has been focused on using cationic dendrimers and polymers for silica synthesis with specific particle size. Our approach is different in that (a) our main focus is silicate solubility enhancement by inhibition, rather than designed silica particle morphogenesis, and (b) we use inorganic silicate for polymerization experiments (not organosilicon starting materials) as a “closer” model to natural systems. Menzel and Behrens have studied the role of synthetic polyamine-like macromolecules on silicate condensation and found that they exert

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an accelerating effect.[21] Colloidal silica with precise structure, particle size, and porosity is of great interest from both a fundamental and applications perspective. Nature creates nanopatterned silica in a precise and reproducible manner using combinations of biomacromolecules. Further insight into these silica formation mechanisms will certainly prove useful in transferring this knowledge to technological and engineering applications.

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Supporting Information Available: Additive chemical structures, FT−IR, XRD powder paterns, and SEM images of a SiO_2−PAMAM-2 composite, graphs showing detailed information on silicate stabilization by PAMAMs. This material is available free of charge via the Internet at http://pubs.acs.org.

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