

Interactions of cationic dendrimers with hematite mineral

Zhonghua Pan^a, P. Somasundaran^{a,b,*}, N.J. Turro^c, Steffen Jockusch^c

^a Industry/University Cooperative Research Center for Advanced Studies in Novel Surfactants, Columbia University, S.W. Mudd, New York, NY 10027, USA

^b School of Engineering and Applied Science, Columbia University, 911 S.W. Mudd Bld, New York, NY 10027, USA

^c Department of Chemistry, Columbia University, 3000 Broadway, Mail Code 3119, New York, NY 10027, USA

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Abstract

Interactions of dendrimers on solid substrates are important in processes involving their coating, flocculation, sedimentation, etc. The adsorption of positively charged poly(amidoamine) dendrimers on hematite/water interface has been investigated in this work as a function of pH, ionic strength, and dendrimer generation by measuring the amount of dendrimers adsorbed and zeta potential changes upon adsorption. Two generations of dendrimers, G3 and G7, were selected, representing “earlier” and “later” generations. At pH 9, the adsorption density of G3 dendrimer on negatively charged hematite increased and reached a plateau with an increase in dendrimer concentration. At pH 4, there is no measurable adsorption of the dendrimer on positively charged hematite in 0.01 M NaCl solutions, and a “negative adsorption” in the distilled water, a condition of a much lower ionic strength showing that the interaction between the hematite surface and the dendrimers is governed mainly by the electrostatic forces. At pH 9, adsorption of G7 dendrimer on hematite is much higher than that of G3 dendrimer and it did not even reach a plateau in the tested dendrimer concentration range, a result consistent with the hypothesis that the adsorbed G7 dendrimers assume a compressed conformation while adsorbed G3 dendrimer molecules take more expanded conformation on the solid. With the increase in the adsorption of G3 dendrimer at pH 9, zeta potential of hematite changed from negative to positive and stayed constant when the adsorption reached a plateau. Clearly, deposition of dendrimers can be controlled by manipulating the interfaces and charge of the solid adsorbent such as hematite.

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1. Introduction

Dendrimers, a class of highly branched synthetic polymers, have unique properties due to their terminal surface functional groups and specific shapes compared with those of the conventional linear polymers [1]. It is important to understand the fundamental interactions of dendrimers with various solids so that their behavior at interfaces can be controlled. Interfacial behavior of dendrimers has received considerable attention recently [2–8], particularly the variation of adsorption properties as a function of dendrimer generation and surface functional groups [2]. In this work, adsorption of poly(amidoamine) dendrimers possessing sur-

face amino groups at the hematite/water interface and corresponding zeta potential has been investigated. Two generations of dendrimers, G3 and G7, were selected, representing “earlier” and “later” generations.

2. Experimental

2.1. Materials

G3 amine-terminated PAMAM dendrimer (32 surface amino groups, Mw: 6909; diameter: 3.6 nm) and G7 amine-terminated PAMAM dendrimer (512 surface amino groups, Mw: 116493; diameter: 8.1 nm) [9,10] were obtained from Dendritech Inc. Hematite was purchased from Alfa Aesar Company and its B.E.T. specific surface area (measured with a Quantasorb sorption system) and particle size were $8.4 \text{ m}^2 \text{ g}^{-1}$ and $<5 \text{ }\mu\text{m}$, respectively. All solutions

* Corresponding author. Tel.: +1-212-854-2926; fax: +1-212-854-8362.

E-mail address: ps24@columbia.edu (P. Somasundaran).

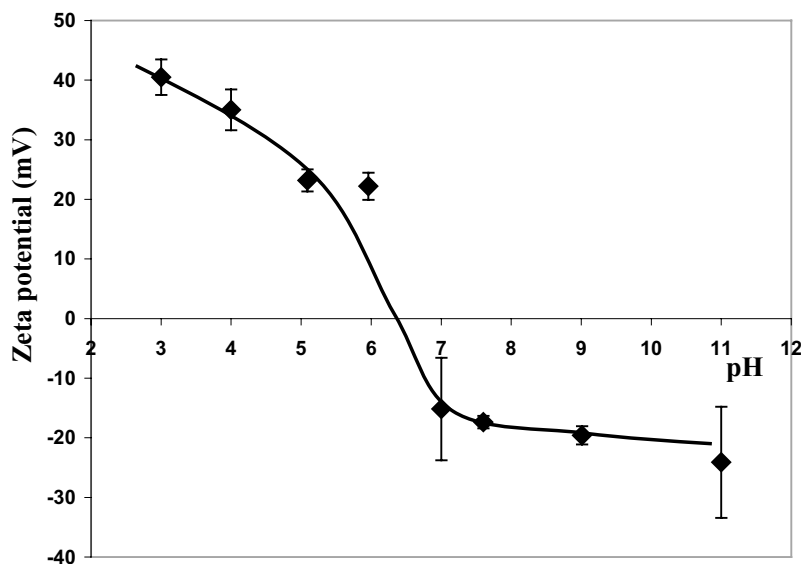


Fig. 1. Zeta potential of hematite as a function of pH. (Hematite particle size $<5 \mu$, Alfa products; I: 0.03 M NaCl.)

were prepared using distilled water. The ionic strength and pH were adjusted with NaOH or HCl.

2.2. Methods and measurements

Aqueous dendrimer solutions were mixed with hematite suspensions in water adjusted to the desired pH value. All the mixed suspensions were stirred in glass vials for 24 h to reach adsorption equilibrium and the pH values were checked and adjusted during the adsorption test. After mixing, the suspensions were centrifuged at 5000 rpm and the concentration of dendrimer in the supernatants was determined using a total organic carbon analyzer (TOC-5000A, Shimadzu). The amount of dendrimers adsorbed on hematite was obtained from dendrimer depletion. Zeta potential of the suspensions was measured using an electrophoresis apparatus (Zeta-Meter 3.0) and an electroacoustic spectrometer (DT-1200 Acoustic and Electroacoustic Spectrometer, Dispersion Technology Inc.). The charge of dendrimer in the aqueous solutions was measured using a Zeta Potential Analyzer Version 2.18 (Brookhaven Instruments Corp.). The reported values are the average of measurements.¹ Error bars (lines) are included.

3. Results and discussion

3.1. Electrophoresis

The amine-terminated dendrimers in aqueous solutions are positively charged in the complete pH range. The positive charge of the dendrimer surface increases with a de-

crease in pH as the result of increasing degree of protonation of the dendrimer surface. For example, the charge of G3 amine-terminated dendrimer is ca +34 mV at pH 4 and ca +25 mV at pH 9. The point of zero charge of hematite is at pH ~ 6.5 (Fig. 1).

3.2. Dendrimer adsorption

Fig. 2 shows the adsorption isotherms of G3 dendrimer on hematite as a function of pH and ionic strength. The adsorption density of dendrimer increased and reached a plateau with increasing dendrimer concentrations at pH 9 in 0.03 M NaCl. At pH 4, the adsorption of dendrimer on the positively charged hematite was close to zero at all dendrimer concentrations in 0.03 M NaCl solutions and negative in water, suggesting that the interaction between the hematite surface and the dendrimers was primarily electrostatic in nature. Adsorption at pH 9 resulted from the attraction between negatively charged hematite surface and positively charged dendrimer, and negative adsorption in water at pH 4 was due to the repulsion between positively charged hematite surface and positively charged dendrimer. Adsorption was close to zero in salt solution at pH 4 as the electrostatic repulsion was minimized by Cl^- counter ions. Such repulsion at pH 4 was much stronger when ionic strength was reduced. Thus interestingly, repulsion between hematite surface and dendrimer in distilled water at pH 4 leads to the dendrimer exclusion in the solution near hematite surface which in turn leads to an increase in concentration in the bulk solution, thus, resulting in “negative” adsorption (Fig. 2).

The effect of dendrimer generation is shown in Fig. 3. It can be seen that adsorption of dendrimer on hematite was higher with higher dendrimer generation (G7) than with lower generation (G3) at pH 9. Dendrimer adsorption has changed the interfacial potential of hematite (Fig. 3). With

¹ Dendrimer concentration and zeta potential were measured 3 to 10 and 15 to 20 times, respectively.

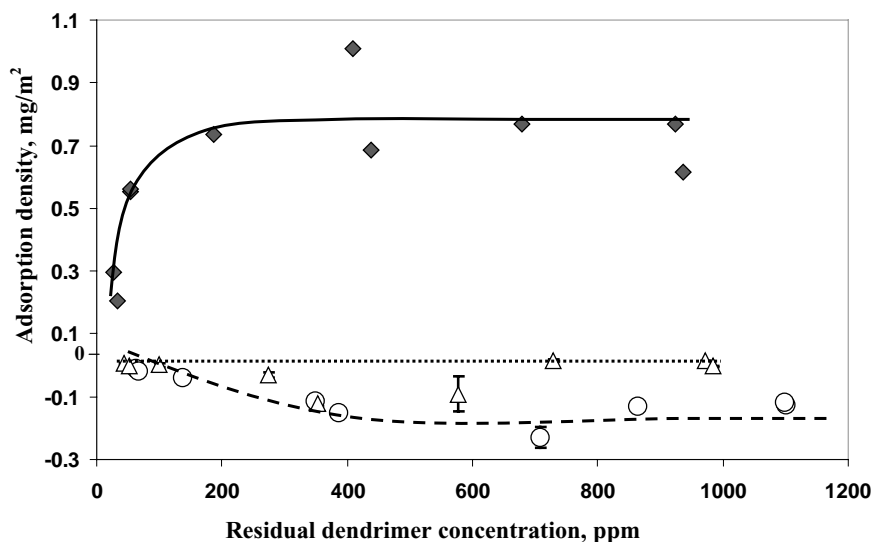


Fig. 2. Dendrimer adsorption on hematite as a function of pH and ionic strength. (Dendrimer Mw: 6909; G3.0; Hematite particle size $<5\ \mu\text{m}$, Alfa products; pH 4; 10 wt.% solid) pH9, I: 0.03 M NaCl (—); pH 4, I: 0.03 M NaCl (.....); pH4, I: distilled water (---).

increase in G3 dendrimer adsorption at pH 9, zeta potential of hematite changed from negative to positive and stayed constant when adsorption reached a plateau. The value at plateau can be considered to represent the zeta potential of dendrimer itself.

Surface coverage of hematite, calculated on the basis of the dendrimer diameters (G3, 3.6 nm; G7, 8.1 nm) at pH 9 is shown in Fig. 4 as a function of dendrimer residual dendrimer concentration. Given close packing (hexagonal or cubic) and no deformation of adsorbed molecules, monolayer adsorption of spherical molecules on solid surface will give a maximum surface coverage of ca 90 and 80%, respectively. Adsorption of G3 dendrimer shows a plateau (see Fig. 3), which corresponds to 70% surface coverage assuming no deformation. This suggests that G3 dendrimer molecules could take a flat/oblate conformation on hematite surface even at saturated adsorption since more surface is available to them.

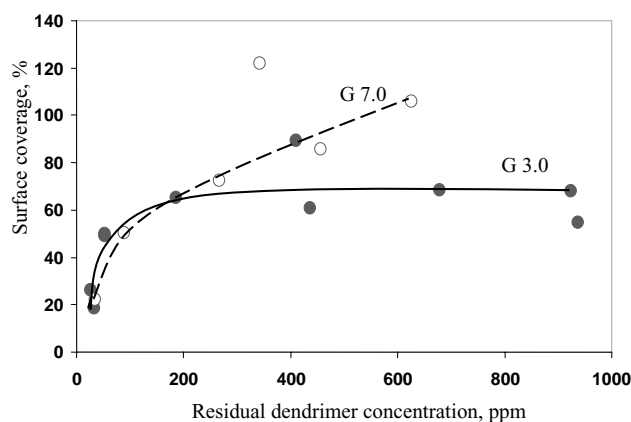


Fig. 4. Surface coverage of hematite as a function of dendrimer generation and concentration. (pH 9, I: 0.03 M NaCl, solids loading: 10 wt.%; G3.0, Mw: 6909, $D = 3.6\ \text{nm}$; G7.0, Mw: 116493, $D = 8.1\ \text{nm}$.)

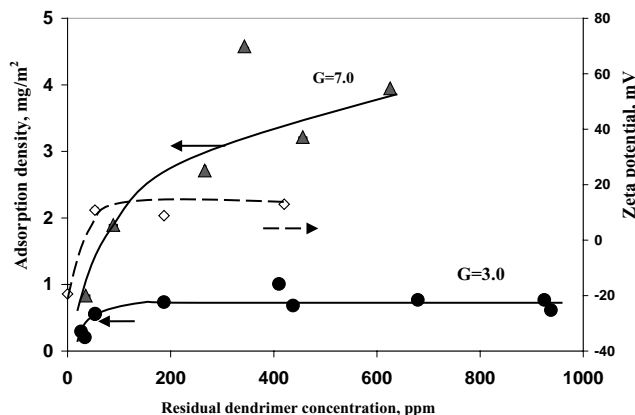


Fig. 3. Effect of dendrimer generation on adsorption and surface charge of hematite as a function of dendrimer concentration. (Dendrimer G7.0, Mw 116493; G3.0, Mw 6909; pH 9, I: 0.03 M NaCl, solids loading: 10 wt.%.)

Adsorption of G7 did not reach a plateau even with a density as high as $3.95\ \text{mg m}^{-2}$ in the tested dendrimer concentration range (see Fig. 3) which corresponds to ca 100% surface coverage assuming no deformation, implying that G7 dendrimer molecules take a compressed conformation on the hematite surface with increase in dendrimer concentration. These calculations are only approximate because of the difficulty in determining the dendrimer diameters and the approximations that are made serve as a qualitative guide to the differences in the adsorption of the earlier and later dendrimers on solid surfaces.

4. Concluding remarks

Interactions between a hematite surface and a dendrimer with net positive surface charge are governed primarily

by the electrostatic forces. Adsorption of dendrimers on hematite at $\text{pH} > \text{pH}_{\text{pzc}}$ is due to electrostatic attraction while repulsion between hematite surface and dendrimer at $\text{pH} < \text{pH}_{\text{pzc}}$ resulted in interfacial exclusion and thus negative adsorption in water, and no measurable adsorption when the repulsion is minimized with salt addition. Adsorption increased with an increase in dendrimer generation. These results are consistent with the dendrimer molecules of a lower generation which take a flat/oblate conformation while dendrimer molecules of a higher generation take a compressed conformation on the hematite surface. There is not enough data or technique to sort out the various possibilities at this time [8,11]. Adsorption of dendrimers modified interfacial potential of hematite suggests their potential for modifying the behavior of solids.

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