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Study of Reconfiguration of Hairs on Mixed Charge Latex Surfaces upon Their Approach to Similarly Charged Host Surfaces: Interaction Force Study Using Atomic Force Microscopy

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Received January 6, 1998. In Final Form: February 10, 1999

Reconformation/reorientation of tethers on particles to minimize the energy of interaction, proposed as the mechanism for their deposition on similarly charged surfaces, has been confirmed using direct force measurements using atomic force microscopy. The force experienced by latex particles of net negative charge on negative glass surfaces, in the presence of the apparent energy barrier based on their ζ potential, is measured to monitor possible rearrangement of surface hairs to enable deposition of zwitterionic latexes while preventing that of the anionic ones.

Introduction

Deposition of particles on surfaces as well as flocculation/dispersion behavior of colloids in suspension is critically dependent on the nature of the forces between the surfaces involved. Predictive models of colloidal stability based upon the balance of van der Waals attraction and electrostatic repulsion as described by Derjaguin–Landau–Verwey–Overbeek (DLVO) theory have been widely reported.^{1,2} However, most models assume a homogeneous static charge distribution and model the particle surface as consisting of either immobile charges (constant charge assumption) or fully mobile charges that equilibrate such that the surfaces maintain a constant potential. Forces in real particulate systems are expected to exhibit a behavior between these two extremes. More importantly, surfaces with charges or adsorption sites on tethers can be expected to reorient as they approach other surfaces so as to minimize repulsion between them, and we propose this to be the reason for the deposition of zwitterionic latex particles with a net negative charge on negatively charged surfaces.³

There is some evidence in many biological systems for surface charges not only forming discrete arrangements on the surface but also being mobile. Modeling these complex effects has been attempted by researchers under certain simplifying assumptions.^{4–7} In this work, direct force measurements, using atomic force microscopy (AFM), between latex particles and glass surfaces in aqueous

Table 1. Specifications of Latex Particles Used

latex type	diameter (μm)	charge group	charge type
		sulfate amidine and carboxyl	anionic mixed

media are used to examine possible rearrangement of the hairy layer leading to the unexpected deposition of zwitterionic latex particles on glass in the presence of an apparent energy barrier estimated using their ζ potentials.

Experimental Section

Materials. Sulfate and zwitterionic spherical latex particles obtained from Interfacial Dynamics Corporation spheres were used as received. These lattices are stabilized in solution by charge groups present on their surface (Table 1). Forces were measured between a 40 μm diameter glass sphere (from Duke Scientific) and a glass microscope cover slide (from Fisher Scientific Company) coated with the latex particles. A cationic polymer, (poly)ethylenimine (average molecular weight, 25 000), was obtained from Aldrich Chemicals and used for coating the glass substrates to facilitate deposition of latex particles.

Methods. Force Measurement. Recently, AFM has been developed as an important tool for force measurements. Following the methodology of Ducker et al.,⁸ forces are measured between a sphere glued to the end of the AFM cantilever and a fixed substrate using a Digital Instrument Nanoscope III. By measuring the deflection of the cantilever as the substrate moves toward and away from it and using the spring constant of the cantilever, the magnitude of the force at a given separation distance may be calculated. Glass spheres were attached to 200- μm -wide contact-mode cantilevers (Digital Instruments) (0.12 N/m approximate spring constant). A monolayer of latex particles were deposited on a glass substrate previously coated with a cationic polymer using a technique described earlier by Somasundaran et al.^{9,10}

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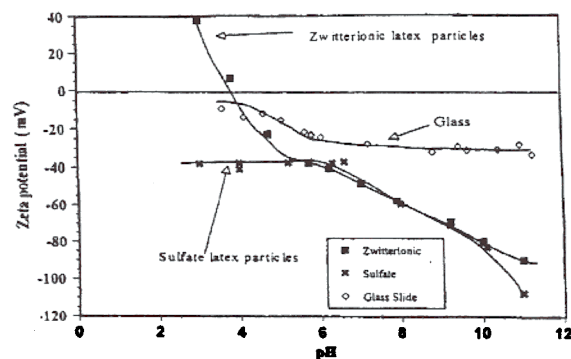


Figure 1. ζ potential of the zwitterionic and anionic sulfate latex particles and glass as a function of suspension pH (ionic strength, 10^{-4} M NaCl).

As-received slides were cut to conform to the size of the AFM sample holder, and the pieces were immersed in a 1:1 nitric acid solution for 2 min and washed with double-distilled water. Cut pieces were then dipped once in a 0.1 wt % cationic polymer solution and rinsed with double-distilled water for 5 min to remove any excess polymer. A drop of latex suspension was transferred to the coated slide pieces and left for free settling for 2 min. The slide was then washed with double-distilled water to remove any free latex particles. Glass slide pieces were then attached on the sample holder using double-sided tape, with the coated surface facing outward. Finally, the aqueous cell was filled and rinsed with double-distilled water at pH 6.

ζ Potential Measurements. Electrokinetic characterization of glass slides was done by measuring streaming potential using a Brookhaven-AP Paar Electrokinetic Analyzer with a rectangular cell holder. Latex particles were characterized using a Pen Kern Lazer Zee meter, model 500. All experiments were performed at room temperature at an ionic strength of 10^{-4} M NaCl.

Results and Discussions

The ζ potential of latex particles and the glass used is shown in Figure 1 as a function of pH. As expected for glass, the substrate is negatively charged throughout the pH range of 3–12. The ζ potential of latex particles show the sulfate latex to be negatively charged under all of the pH conditions studied and the zwitterionic latex particles to possess an isoelectric point around pH 4 (Figure 1). At pH 6, where the previous deposition tests and present force measurements are performed, both sulfate and zwitterionic particles have similar ζ potentials (~ -40 mV). The force-distance profiles between the sulfate and zwitterionic latex particles and the glass surface are shown in Figure 2. Because all surfaces under these pH conditions are negatively charged, an electrostatic repulsion barrier is expected. The measured force for the interaction of sulfate latex particles and glass is as expected. As the glass sphere approaches the latex film, the repulsive force increases until, at short separation distances, attractive contributions from van der Waals forces cause a decrease in the repulsion. At this point, the cantilever jumps into contact with the surface and little change in distance is seen with additional applied pressure.

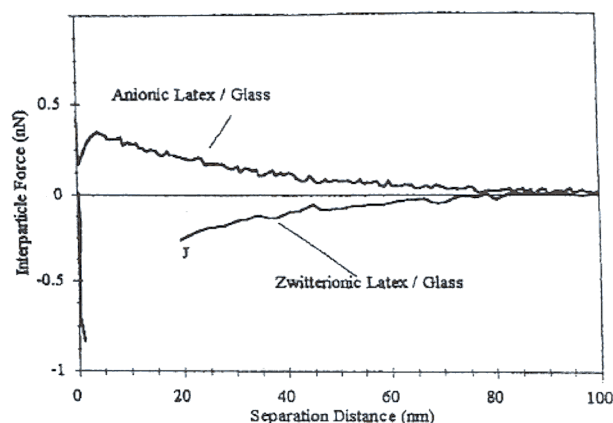


Figure 2. Force/distance profile of glass surface and zwitterionic and anionic sulfate latex particles in water at pH 6. J indicates approximate position of the point of mechanical instability where the attractive forces exceeded the spring constant of the cantilever and the surface "jumped" into contact.

However, the force profile for the zwitterionic latex particles is different from that of the sulfate latex particles. In spite of having an overall ζ potential similar to that of the sulfate latex, zwitterionic lattices show no repulsion; instead, a net attraction is observed. Force calculations based on uniform charge distribution and overall ζ potential do not account for the presence of an attractive force; and a proposed rearrangement of the hairs in the mixed-charge layer on zwitterionic latex particles is considered responsible for the attraction. It is proposed that the charges on the latex surface in the presence of another negatively charged surface rearrange in such a manner that the positive charge sites are extended and the negative ones are retracted. Thus, even though the measured net ζ potential of the zwitterionic particles is negative, reconfirmation of the hairs in the charged layer takes place when the two surfaces begin to feel each other permitting their attachment to the negative glass surface.

In summary, the experimental evidence presented in this work clearly confirms the role of the discrete nature of charges in colloidal force calculations and supports the proposed selective reconfirmation or reorientation mechanism of the hairs to minimize the energy of interaction between two surfaces which have similar "net" charges. Deposition of particles with attachment or deposition of particles on similarly and dissimilarly charged surfaces is thus possible due to reconfirmation of tethers.

Acknowledgment. The authors acknowledge the financial support of Unilever Research and the Engineering Research Center (ERC) for Particle Science and Technology at the University of Florida, the National Science Foundation (NSF) Grant #EEC-94-02989, and the Industrial Partners of the ERC.

LA980012M