Supporting Information

Electrostatically controlled swelling and adsorption of polyelectrolyte brush-grafted nanoparticles to the solid/liquid interface

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Implementation of the Electrostatic Random Sequential Adsorption Model

The influence of pH on SiO_2-*g*-PDMAEMA adsorption was captured qualitatively using the electrostatic RSA scaling model developed by Oberholzer and coworkers.[34] This section describes our implementation of their model. The model considers how long-range lateral electrostatic repulsions between rigid charged spheres decrease the jamming limit relative to the uncharged hard sphere jamming limit as the spheres undergo random sequential adsorption to an attractive surface. The model is used to predict the radius R_{ex} of the excluded area for a particle of radius R according to the strength and range of the electrostatic repulsions between particles. The Yukawa potential is used to estimate the ratio R_{ex}/R:

$$U_c = \frac{\overline{N} B_{pp}}{2\left(\frac{R_{ex}}{R}\right)} e^{-2\kappa R[(R_{ex}/R)-1]} \tag{S1}$$

where U_c is the maximum allowable energy penalty for successful adsorption, $\overline{N}$ is the number of nearest neighbors, and B_{pp} is the Yukawa coefficient for particle-particle electrostatic repulsions:

$$B_{pp} = \left(\frac{4\pi k_B T \epsilon \epsilon_0 R}{e^2}\right)\left(4\gamma + \frac{2}{\kappa R}\gamma^3\right)^2 \tag{S2}$$

Here, $\gamma = \tanh(\tilde{\psi}_p/4)$ and $\tilde{\psi}_p = \psi_p e/k_B T$ is the dimensionless particle surface potential. For the purpose of interpreting trends in the adsorption of SiO$_2$-g-PDMAEMA with respect to pH changes, we emphasize the basic ideas concerning the importance of long-range electrostatic repulsion among soft charged spheres using electrostatic RSA. The original model was strictly developed for rigid charged spheres. We used dynamic light scattering results to set $R = R_h$ and electrophoretic mobility measurements to approximate the surface potential by equating $\psi_p = \zeta_{p,app}$ to calculate B_{pp}. Unlike the rigid spheres treated by the original model, both the potential and the size are pH dependent for SiO$_2$-g-PDMAEMA. Following Oberholzer and coworkers, we assume $\bar{N} = 6$ nearest neighbors and a reasonable estimate of the adsorption barrier $U_c = 1\ k_B T$ in order to estimate R_{ex}/R at each pH using equations (S1 and S2). The area fraction surface coverage at the jamming limit by charged spheres is predicted relative to the neutral hard sphere RSA jamming limit θ_{hd} as

$$\theta_{E-RSA} = \theta_{hd} \left(\frac{R}{R_{ex}}\right)^2 \tag{S3}$$

Simulations with uncharged rigid spheres indicate that $\theta_{hd} = 0.547$. Once the electrostatic RSA jamming limit is calculated, the surface excess concentration is calculated using the BGNP mass and its measured size. Surface excess concentrations estimated in this manner were plotted in the inset of Figure 5 for 1 mM NaCl in the article to which this Supporting Information document is linked.

Reference

S1. Oberholzer, M.; Stankovich, J.; Carnie, S.; Chan, D.; Lenhoff, A. 2-D and 3-D Interactions in Random Sequential Adsorption of Charged Particles. *J. Colloid Interface Sci.* **1997**, *194*, 138–153