

Supplementary Information

Adsorption of polyelectrolytes to like-charged substrates induced by multivalent counterions as exemplified by poly(styrene sulfonate) and silica

Alberto Tiraferri^{1,2}, Plinio Maroni², Michal Borkovec^{2,*}

¹Department of Environment, Land, and Infrastructure Engineering, Polytechnic University of Turin, Torino, Italy

²Department of Inorganic and Analytical Chemistry, University of Geneva, Sciences II, 30 Quai Ernest-Ansermet, 1205 Geneva, Switzerland

*Corresponding author. Email: michal.borkovec@unige.ch

Experimental Details

Sodium polystyrene sulfonate (PSS) of different molecular masses was purchased from Polymer Standards (Mainz, Germany). The polydispersity index was below 1.20. Silica substrates were purchased from LoT Quantum Design (Darmstadt, Germany). These substrates consist of a silicon wafer that was sputter coated involving an adhesion layer of titanium and an upper layer of silica (Fig. S1). The thickness of the silica layer was 34 ± 5 nm, while that of the adhesive titanium layer was approximately 2 nm, as determined by ellipsometry (Multiskop, Optrel, Berlin, Germany). The substrates were similar to the ones used in previous work.¹ The thickness of the silica layer remained constant during the experiments, as was established by measuring its thickness by ellipsometry after the experiments again. The roughness of the silica surface was analyzed by atomic force microscopy (Cypher, Asylum Research, Santa Barbara, CA) in amplitude modulated mode. The root mean square (RMS) roughness of the surfaces was about 0.9 nm.

Prior to use, surfaces were treated using an oxygen-enriched UV-ozone cleaner for 20 min followed by immersion in 2 wt% sodium dodecyl sulfate (SDS) for 30 min; they were then rinsed with water, and finally dried in a flow of nitrogen before another 20 min cleaning cycle in the UV-ozone chamber. Milli-Q (Millipore) water was used throughout. Just before each experiment, the substrates were treated for 20 min with cold piranha solution, which is a 3:1 mixture by volume of H₂SO₄ 98% and H₂O₂ 30%, and washed thoroughly with water. Experiments could be well reproduced on the same surfaces following cleaning.

The surfaces were mounted in an impinging jet cell into which the solution was injected through a 0.5 mm radius bore hole in a capped prism. A linearly polarized green diode laser with a wavelength of 532 nm was pointed at this stagnation point with a final angle of incidence on the surface of roughly 71°, where light refraction in the prism was considered. The reflected laser beam from the adsorbing surface was split into its parallel and perpendicular polarization components. The ratio of the intensities of the split beams R is proportional to the ratio of the reflectances for the field perpendicular and parallel to the reflection plane. The adsorbed dry mass Γ was determined from

$$\Gamma = \frac{1}{A} \cdot \frac{R(t) - R(0)}{R(0)} \quad (1)$$

where A is a sensitivity constant. This constant was calculated from a four-slab model, in which the upper fourth slab corresponded to the adsorbed polyelectrolyte layer. The appropriate refractive indices for silicon $4.14 - 0.01i$, titanium $2.48 - 2.00i$, and silica 1.457 were used. They were obtained from <http://refractiveindex.info/>. The ideal mixing law was used to obtain the refractive index of the solution

$$n_{\text{sol}} = n_w + \frac{dn}{dc} \cdot c \quad (2)$$

where $n_w = 1.334$ is the refractive index of water and c the molar salt concentration. Similarly the refractive index of the polyelectrolyte layer

$$n_p = n_s + \frac{dn}{dc_p} \cdot \frac{\Gamma}{L} \quad (3)$$

where c_p is the mass concentration of PSS and L is the thickness of the polymeric layer, which assumed to be 1 nm. The precise value of L does not affect the results. The refractive index increments were determined with a refractometer at a wavelength of 532 nm (Abbemat, Anton Paar, Austria) for aqueous solutions of LaCl_3 and PSS. They were 46.9 mL/mol and 0.156 mL/g, respectively. The latter value was independent of molecular mass. The refractive index increments of MgCl_2 and NaCl are 20.8 mL/mol and 9.94 mL/mol as reported elsewhere.² In this study, the sensitivity factor ranged between 0.045 and 0.055 m^2/mg depending on the solution chemistry. All experiments were carried out at room temperature of $21 \pm 3^\circ\text{C}$.

References

- 1 M. Porus, P. Maroni and M. Borkovec, *Langmuir*, 2012, **28**, 5642-5651.
- 2 M. Porus, C. Labbez, P. Maroni and M. Borkovec, *J Chem Phys*, 2011, **135**, 064701.

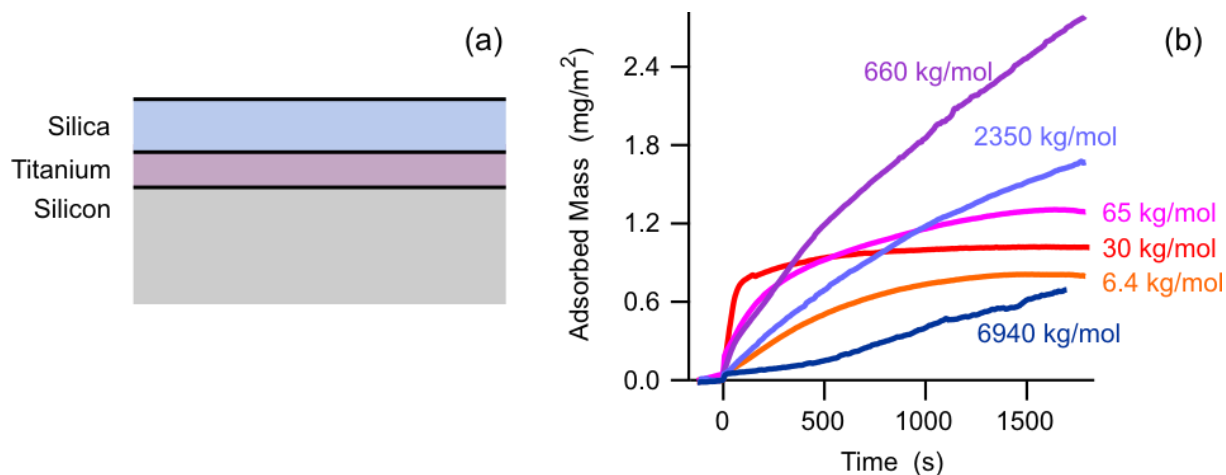


Figure S1. (a) Scheme of the substrate used for the adsorption studies. Not to scale. (b) Adsorption traces of PSS of different molecular mass. The experiments were conducted in a 300 mM LaCl_3 solution of pH 6.0. PSS of a concentration of 10 mg/L was introduced at time zero.