

Interaction of sodium dodecyl sulfate and high charge density comb polymers at the silica/water interface

Moglianetti et al.

Supplementary Information

Experimental method: ellipsometry

The ellipsometry measurements were performed with a modified, automated Rudolph Research thin-film null ellipsometer, model 43603-200E, equipped with high precision step motors and controlled by a personal computer. The instrument was set up in polarizer, compensator, sample and analyzer arrangement. The light source was a xenon arc lamp, using an interference filter to obtain a wavelength of 4015 Å. The angle of incidence ϕ was set at 68° to obtain the best sensitivity under our experiment conditions.

The silicon was thermally oxidized in pure oxygen at 920 °C for an hour, followed by cooling in an argon flow. This procedure produces a SiO₂ layer with a thickness of 30 nm. The wafers were cut into slides and then cleaned (i) for 5 min in boiling mixtures (1:1:5 by volume) of 25% NH₄OH (pro analysi, Merk), 30% H₂O₂ and H₂O, (ii) for 10 min in boiling mixtures (1:1:5 by volume) of 32% HCL (pro analysi, Merk), 30% H₂O₂ and H₂O. After this procedure the slides were rinsed again with water and stored in 99wt% ethanol. Before use the surfaces were dried in nitrogen flow and plasma cleaned for 5 minutes in radio frequency plasma (Harrick Scientific Corp., Model PDC-3XG) in residual air at 0.03mbar at a power of 30W.

To obtain reliable measures of the refractive index and thickness of the adsorbed film, the optical characteristics of the substrate (Si/SiO₂ plates) must be determined at the beginning of each experiment. The substrate is assumed to consist of bulk silicon with a complex refractive index, $\hat{n}_2$, and a layer of silica with refractive index n_1 and thickness d_1 , surrounded by a transparent medium with refractive index, n_0 . The optical properties of the oxidized silicon substrate were obtained by measuring Ψ and Δ in two ambient media, air and electrolyte solution. When these parameters are known, it is possible to calculate the complex refractive index ($\hat{n}_2 = n_2 + jk_2$) of the bulk silicon and the thickness (d_1) and the refractive index (n_1) of the silica layer. Typical values of these parameters are $n_2 = 5.5 \pm 0.01$, $k_2 = -0.35 \pm 0.03$, $d_1 = 300 \pm 20$ Å and $n_1 = 1.480 \pm 0.005$.

The cuvette was equipped with Teflon tubes and the solution in the cuvette could be changed under well-defined flow rate without emptying the cuvette, by means of a multi-channel peristaltic pump. Agitation was achieved by means of a magnetic stirrer at 100 rpm.

The changes in Ψ and Δ in one zone were recorded as a function of time and were corrected for optical imperfections using the data from the four zone measurements of the substrate. After each injection, the measurements were conducted until no further changes in the ellipsometric angles were detected (typically 15-20 min). The recorded values of Ψ and Δ were evaluated using a four layer optical model, assuming isotropic media and planar interfaces.

Table S1: Scattering length densities for the different species used in this study.

Material	$\rho_l/(10^{-6} \text{ \AA}^{-2})$
Si	2.07
SiO _x	3.5
D ₂ O	6.35
<i>h</i> -SDS	0.4
<i>d</i> -SDS	6.7
METAC	0.76
EO ₄₅	0.57
PEO ₄₅ MEMA:METAC-90	0.67
PEO ₄₅ MEMA:METAC-75	0.64

Figure S1: Scattering length density profiles obtained for (left) PEO45MEMA:METAC-90 interacting with 0.35 mM and 2.5 mM *h*-SDS and *d*-SDS in D₂O and (right) PEO45MEMA:METAC-75 interacting with 0.29 mM and 2.1 mM *h*-SDS and *d*-SDS in D₂O.

