

Salt-Controlled Self-Assembly of Triblock Copolymers-F68 on

Interaction Forces between Oil Drops in Aqueous Solution

Hang Jin[†], Wei Wang^{*†}, Hongli Chang[†], Yun Shen[†], Zhipeng Yu[†], Yunya Tian[†], Yang Yu[†] and Jing Gong^{*†}

Supporting Information

■ Ellipsometry Measurement

Thickness (337.1 ± 0.4 nm) of the silica layer covered on silicon wafers were measured by ellipsometry at $20 \pm 0.5^\circ\text{C}$, under wave lengths of spectroscopic light sources from 360 nm to 1000 nm with a incidence angle of 50° . This technique measures the change of the polarization state (parameters Δ and Ψ) of a light beam upon reflection at an interface, as shown in Fig. S1. Then the thickness of the silica layer can be obtained by nulling through the software.

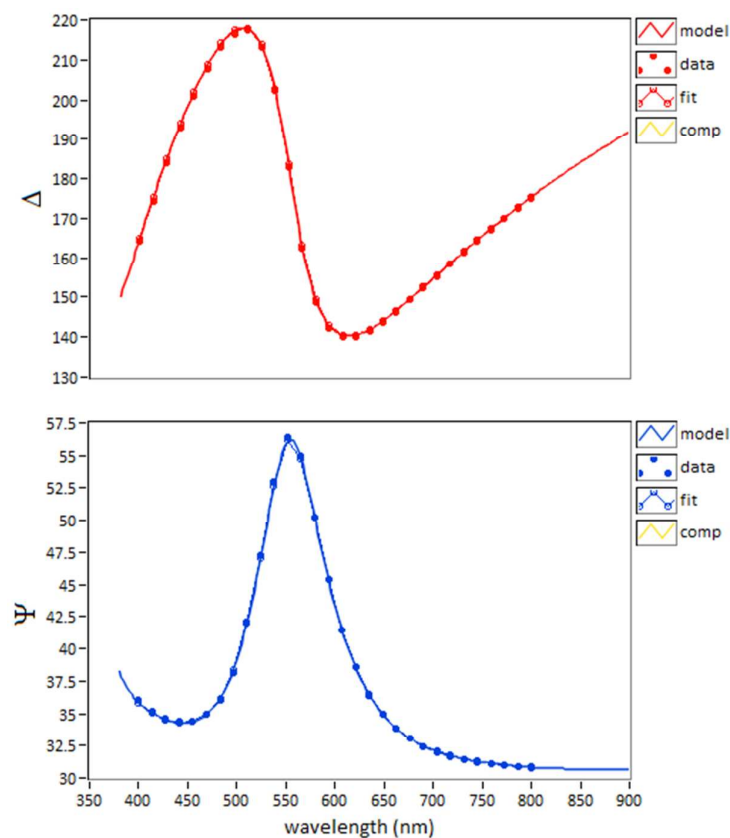


Figure S1. Polarization state (Δ and Ψ) under different wave lengths of spectroscopic light measured by ellipsometry at $20 \pm 0.5^\circ\text{C}$.

■ Contact Angle Measurement

The contact angles of tetradecane drops increased with the increasing concentration of F68 solutions from 0 to 500 μM (20 mM NaCl), as shown in Fig. S2A. The addition of F68 was found to reduce the degree of hydrophobicity of the

substrate, consequently increasing the contact angle¹. However, the contact angles decreased with the increasing salinity (≥ 100 mM) at the same copolymer concentration (500 μM), as shown in Fig. S2B. The addition of NaCl diminishes the adsorption of F68 molecules on silica surface but enhances the precipitation of F68 aggregates on surface which imposes a complex influence on the hydrophobicity of the substrate. The sensitivity of drop interaction forces to contact angle changes were simulated with the limiting case for droplet deformation²(see Eq. (1)).

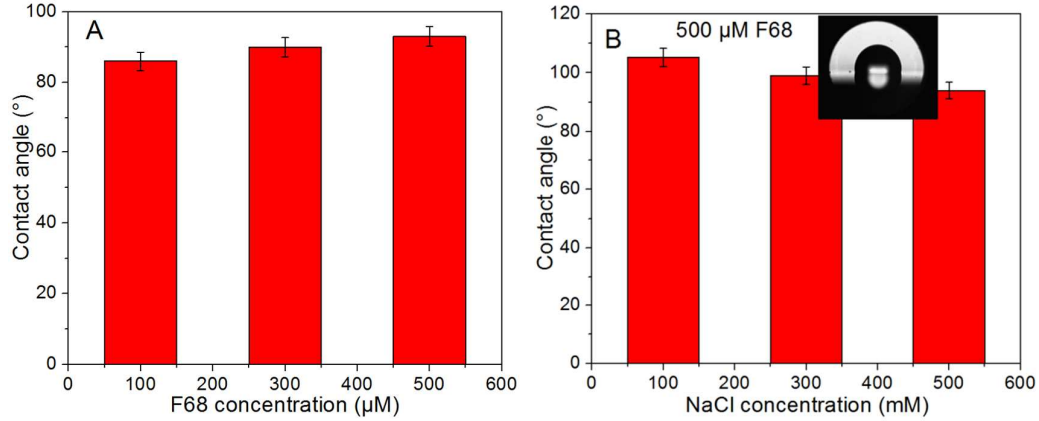


Figure S2. Contact angles of tetradecane drops formed on the silicon wafers measured in solutions (A) with increment of F68 concentrations from 100 to 500 μM and (B) with increment of NaCl concentrations from 100 to 500 mM (500 μM F68).

■ Sensitivity of force curve

The measured force curves after washout are simulated with the limiting case for droplet deformation². But for the case before washout, it's very hard to model the force curve in detail because of the trapped copolymers or aggregates between interacting drops. The complex interacting mechanisms between trapped copolymers or aggregates impose a much more complicated effect on drop interaction.

$$\Delta X \cong h_f + \frac{F}{2\pi\sigma} \left[\log \left(\frac{F}{8\pi\sigma\sqrt{R_C R_S}} \right) + B(\theta_C) + B(\theta_S) - 1 + \frac{2\pi\sigma}{K} \right] \quad (1)$$

Where R_C is the radius of droplet on cantilever and R_S is the radius of droplet on substrate. θ_C and θ_S are the contact angles of droplets on cantilever and substrate, respectively. σ is the equilibrium interfacial tension of oil-aqueous solution interface. ΔX is the drop displacement. h_f is the constant film thickness when the drop surface come into contact with deformation.

The interfacial tension changes caused by desorption after washing the drops in our experimental system are measured to be lower than 1.5 mN/m. From the modelling results, it's found that the minor change of interfacial tension (± 1.5 mN/m) has less impact on the interaction forces.

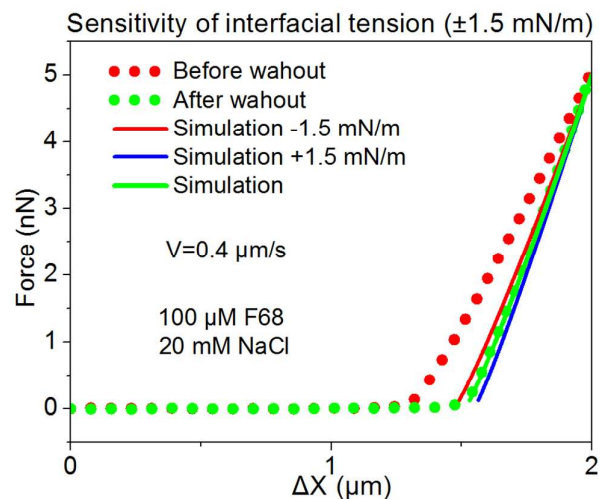


Figure S3. Sensitivity of force curves to interfacial tension changes (± 1.5 mN/m).

And the effects of drop contact angle changes ($\pm 10^\circ$) on the force curves are also simulated, as shown in Fig. S4. The results show that the change in force curve caused by contact angle changes ($\pm 10^\circ$) is rather small.

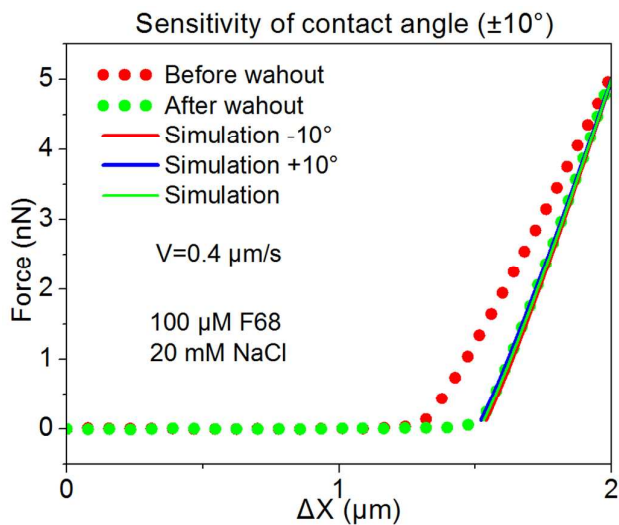


Figure S4. Sensitivity of force curves to contact angle changes ($\pm 10^\circ$).

■ References

- [1] Lockie, H. J.; Manica, R.; Stevens, G. W.; Grieser, F.; Chan, D. Y. C.; Dagastine, R. R. Precision AFM Measurements of Dynamic Interactions between Deformable Drops in Aqueous Surfactant and Surfactant-Free Solutions. *Langmuir* 2011, 27 (6), 2676. DOI 10.1021/la1049088.
- [2] Manica, R.; Connor, J. N.; Dagastine, R. R.; Carnie, S. L.; Horn, R. G.; Chan, D. Y. C. Hydrodynamic forces involving deformable interfaces at nanometer separations. *Physics of Fluids* 2008, 20 (3), 2912. DOI 10.1063/1.2839577.