Structural Forces in Soft Matter Systems - Supporting Information

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Sodium dodecyl sulfate (SDS) as obtained from Sigma (Ultra grade - 99%) and used as received. Perfluorooctane (PFO, 98%) and tetradecane (99%) were obtained from Aldrich and each purified by column chromatography over silica (Florisil, Sigma, 100-200 mesh). Deionised water was from a Milli-Q system, minimum resistivity 18.4 MΩ cm^{-1}. Mica was freshly cleaved from 12 mm discs obtained from ProSciTech (Australia), and used immediately. Before use, all glass surfaces were cleaned by soaking for an hour sequentially in 10% Ajax detergent, then 10% nitric acid, and finally 10% sodium hydroxide, each step being followed by rinsing with copious amounts of deionised water. Pentan-1-ol (99.5%) was from Fluka and used as received. 1-decanethiol (96%) was obtained from Aldrich and used as received.

Rectangular silicon AFM cantilevers (450 × 50 × 2 μm were custom made, with a circular ‘gold coin’ (diameter 45 μm, thickness 20 nm - shown schematically in inset to Figure 1 of the main paper) added ≈5 μm from the end by focused ion-beam deposition.[1,2] This allowed the contact area of the bubbles on the cantilever to be precisely known. This area was rendered hydrophobic by reaction with 1 mM decanethiol in absolute ethanol for 20 minutes. Cantilever spring constants, K, were determined by the method of Hutter and Bechhoeffer.[3] The AFM measurements were performed on an Asylum MFP-3D AFM, equipped with a linear variable differential transformer (LVDT) sensor in the Z-movement direction, to allow direct detection of cantilever Z-position during force measurements. This has been shown to be vital for accurate force-displacement measurements, as piezo spontaneous velocity is non-linear.[1]

Droplet radii were measured microscopically (Nikon Ti2000), Debye lengths were calculated from solution compositions (assuming the degree of ionization of SDS to be 0.27[4]), and literature values for the surface potentials for silica and mica were used.[5] Because the effective electrolyte concentration from dissociated SDS was relatively high (65 mM for a bulk concentration of 240 mM SDS), the contribution to the pressure between interacting surfaces from electrical double-layer interactions was effectively sufficiently short-range to be completely masked by the contribution from the structural interaction. The contribution to the interaction from the Van der Waals force was calculated using a full retarded Hamaker function, obtained by the method of Lifshitz, but this was also short-range, and hence masked by the presence of the structural pressure.

Silica particle cantilevers were prepared from regular V-shaped cantilevers (MLCT, Veeco probes). The end of the cantilever was brought down into a small amount of epoxy (Araldite Rapid) and this was used to pick up a silica bead of radius 10μm (Thermo Particle Size Standards). The glue was left to dry for 24 hours before the cantilever was used.

PFO drops generated by gently discharging a glass syringe of the oil under water to give a coarse emulsion with a range of droplet sizes. The substrate used was a glass Petri dish which had been boiled for 3 hours in absolute ethanol,[6] generating a slightly hydrophobic surface suitable for anchoring of bubbles (water contact angle 40 degrees). The volume of water added initially was 4 ml. A suitably sized droplet of PFO was then picked up on the AFM cantilever, and the solution adjusted by addition of 4 ml of concentrated surfactant solution or a microemulsion to the desired concentration, giving a total liquid volume of 8 ml. After equilibration, interactions were measured between the drop and either another drop immobilised on the surface, or a mica flat. Video microscopy was used to measure droplet sizes. The AFM setup was scrupulously cleaned between experiments to ensure no surfactant or other contaminant remained.

Interfacial tensions for PFO-SDS solution and PFO-microemulsion systems were measured using the pendant drop method, utilizing a Dataphysics OCA tensiometer. A pendant drop of PFO was generated in solution and allowed to equilibrate for 20 minutes. After this time, it was photographed, and the profile of the drop perimeter fit to the Young-Laplace equation using the proprietary instrument software, providing the interfacial tension. These values were found to be 15 ± 2 mN/m for PFO-SDS (400 mM), 15 ± 2 mN/m for PFO-SDS (240 mM), and 11 ± 2 mN/m for PFO-microemulsion.

Because of the coupling of the deformable drop and the cantilever spring, both respond to changes in the gradient of the force as separation is changed. During approach with an attractive interaction, both the cantilever and the drop will deform in the approach direction. This will occur smoothly and reversibly until the force gradient has exceeded dF/dX (see e.g. Fig 1 of the main paper), which incorporates the response of the coupled system of the cantilever and drop. At this point a jump-in event will occur. The jump-in will be manifested as a sudden change in the displacement of the cantilever or in the deformation of the drop, or more generally in both, as the two are coupled.

References

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