In-situ Quantitative Study of the Phase Transition in Surfactant Adsorption Layers at the Silica-Water Interface using Total Internal Reflection Raman Spectroscopy

Supporting information

1.   Penetration depth calculation of Raman probe under total internal reflection geometry

When an electric field E of wavelength λ is incident to the interface from an optically denser medium (n_i) at an angle θ larger the critical angle, an evanescence field is generated at the interface and propagates along the interface with the penetration depth into the less dense medium (n_t) is calculated as below[1]

$$d_p = \frac{\lambda}{2\pi\sqrt{n_i^2 sin^2(\theta) - n_t^2}}$$

In this work, the calculated effective penetration depth is ~100 nm, which is not a real surface sensitive technique; however, regarding the aqueous surfactant solutions, the surface density is many order of magnitude higher than in solution, so the bulk contribution is safely neglected or could be calibrated since the bulk contribution will have a linear relationship with the its Raman intensities. Herein, the DDAO solution concentrations are in the order of tens of micro-molarity, so the contribution from bulk is insignificant.

2.   Langmuir-Blodgett (LB) monolayer deposition

1,2-dilauroyl-sn-glycero-3-phosphocholine (DLPC), 1,2-Distearoyl-sn-glycero-3-phosphocholine (DSPC) (Avanti Polar Lipids, Inc) and chloroform (Sigma Aldrich) were used as is. 1 mM of DSPC and DLPC solutions are prepared in chloroform. The silica prism is treated with piranha solution ($HNO_3:H_2O_2$ 4:1) for 1 h and rinsed with copious amount of milli-Q water before the deposition to ensure the surface to be clean and hydrophilic. The formation of the lipid monolayers is carried out by the Langmuir Blodgett method in a LB trough with a Wilhelmy balance (KSV NIMA). The milli-Q water is used as the subphase at 26 ± 1 °C and the compression rate is 5 mm min^{-1}. The surface pressure is hold at the desired surface pressure for 5 minutes before deposition. DSPC and DLPC LB films are deposited onto hemispherical prism with Langmuir-Blodgett method at surface pressure of 45 mN m^{-1} and 35 mN m^{-1}, yielding the area per molecule of 39 Å^2 and 43 Å^2, respectively, based on the isotherms in Figure S1.

The LB monolayers were transferred at high surface pressures as LB transfer requires strong cohesion of the lipids.[2] The transferred LB monolayer is characterized by the transfer ratio, τ (also called deposition ratio) which is the ratio between the change of the monolayer occupied area and the coated area of the substrate.[3] A withdrawing speed at 1 mm min^{-1} was chosen for both of the monolayers to ensure a high transfer ratio (τ = 0.9-1.0).[4–6]
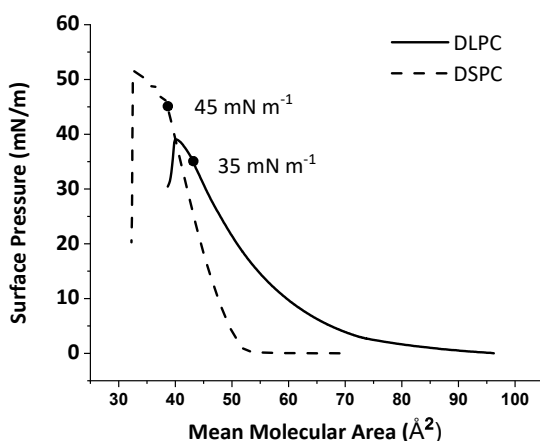

Figure S1: The surface pressure – area (π- A) isotherms of DSPC and DLPC at the air- water interface (26 ± 1 °C). Langmuir-Blodgett DSPC and DLPC monolayers are transferred at 45 mN m^{-1} and 35 mN m^{-1}, respectively.

3.   CTAB adsorption

By performing the same calculation as in part 3.1 with the adjusted fractionalized surface density for C16 chain length, the surface excess of CTAB once the bulk concentration is in the plateau end of the isotherm is computed at 3.1 µmol CTAB m^{-2} with 75% surface coverage. This result is slightly different from the combination of wall-jet model and the convection-diffusion model calculation previously performed by C. Bain et al,[7] showing the computed saturated surface density of CTAB at the silica-water interface is 5.5 µmol m^{-2} by applying diffusion-convection model. However, this calculation required many assumptions and experimental parameters. As compared with DDAO adsorption saturation at 0.77 Γ_{max}, CTAB surface aggregate structures would be less tightly packed and expected to desorb faster than DDAO surface aggregate. Figure S2 reinforces this assertion by showing the slow decrease vs sharp exponential decay in Raman signals at various bulk concentrations of DDAO and CTAB once the solutions are flushed out and replaced by milli-Q water at the same pH ~ 7.5.

(a)   (b)
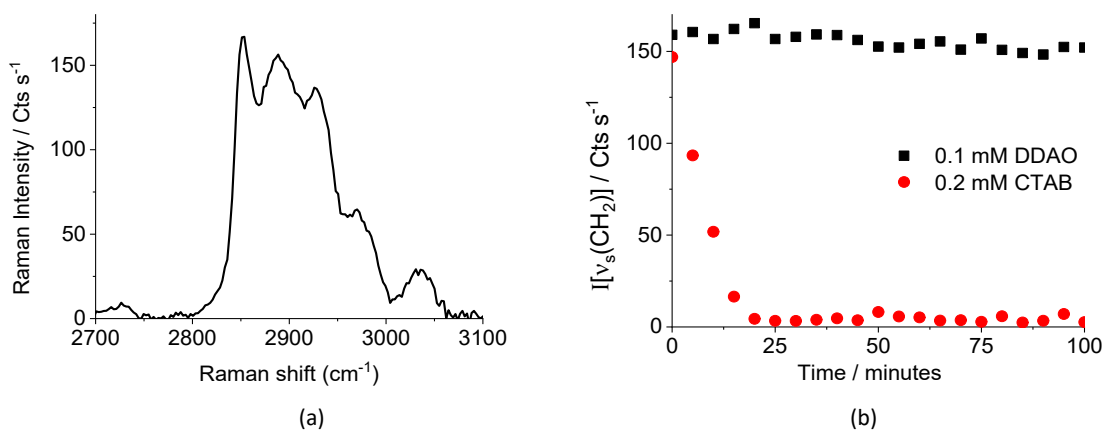
Figure S2: (a) TIR-Raman spectra of 5 mM CTAB, and (b) a simple desorption test to illustrate the high surface affinity of DDAO onto silica surface vs CTAB even though CTAB headgroup carries positive charge and is expected to bind strongly to the silica surface decorated with negative charges.
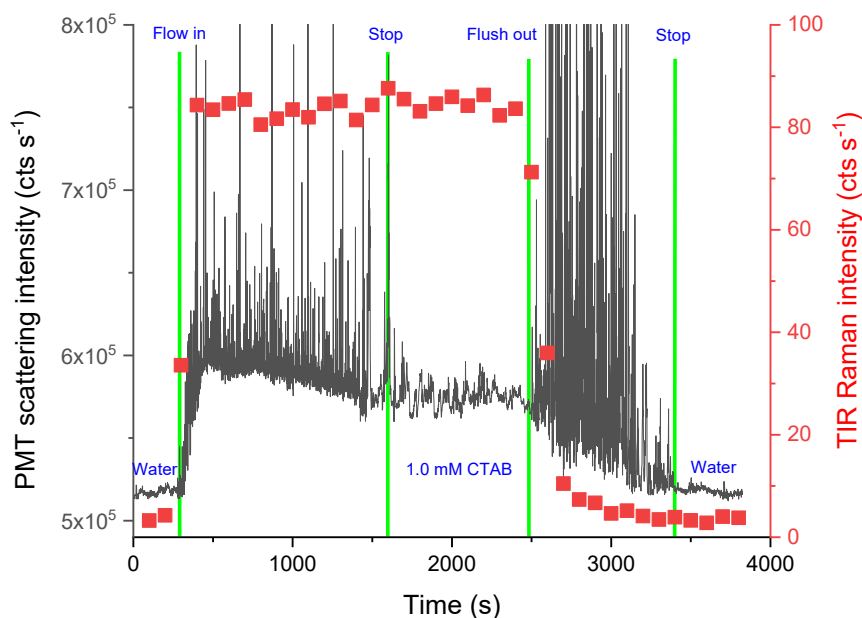

Figure S3: turbidity and TIR Raman simultaneous measurement of 1.0 mM CTAB to illustrate the sensitivity of this system in detecting micelle formation. Below its cmc, there is no significant increase in the turbidity measurement.

4. Critical micelle concentration as a function of temperature
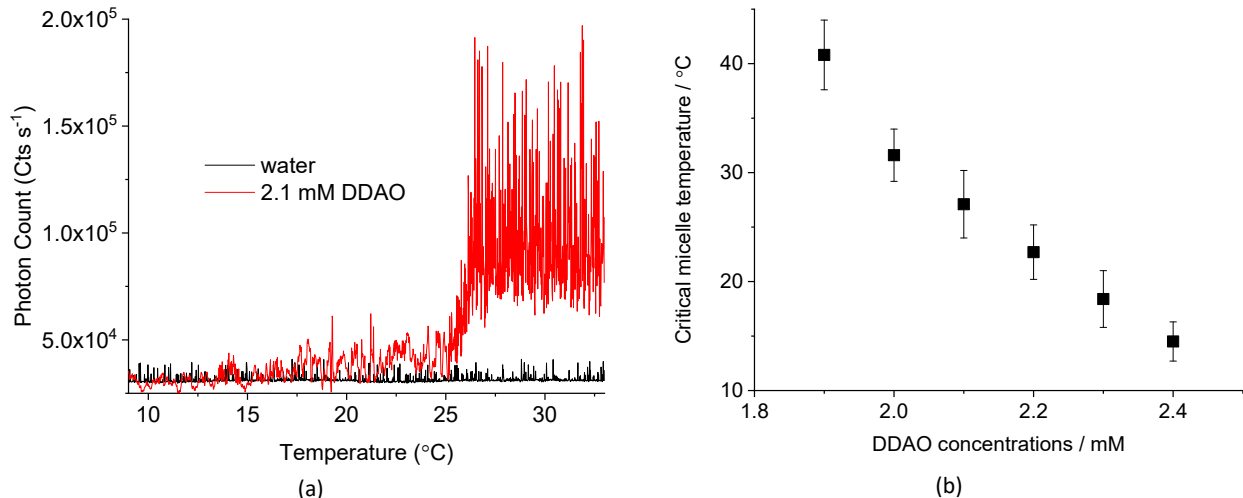
(a)

(b)

Figure S4: (a) illustration of cmc determination as a function of temperature using light scattering (turbidity) method. A known DDAO concentration solution is injected into the fluorescence cuvette and the fluctuation in light scattered at 90° is observed as a function of temperature. Micelles are formed once the temperature of the heated solution exceeds a certain value, called critical micellization temperature (cmt). (b) DDAO cmc values as a function of temperature executed by repeating (a) for various DDAO concentrations.

5. $\Delta G°$, ΔA**, and ΔE relation**

Standard Gibbs free energy is defined as

$\Delta G° = \Delta H - T\Delta S$

where ΔH, T, and ΔS is the energy change (kJ.mol⁻¹) at isobaric condition, temperature (K), and change in entropy (kJ.mol⁻¹.K), respectively. And, Helmholtz free energy is given by

$\Delta A = \Delta E - T\Delta S$

where ΔE is the energy change (kJ.mol⁻¹) at isothermal condition.

In this study, both pressure and volume are constants, which indicate the two form of free energies are used interchangeable, and the change in internal energy are approximately identical, $\Delta E \approx \Delta H$. Then,

$\Delta G° = \Delta A = \Delta E - T\Delta S$

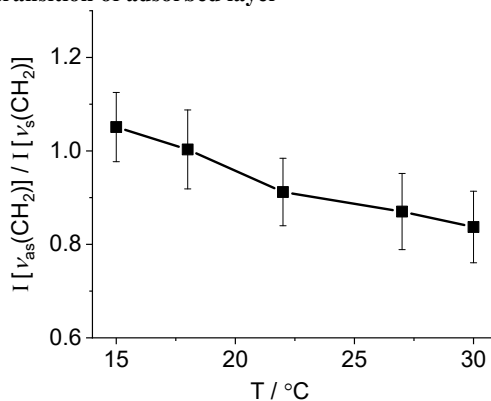**6.   Temperature-dependent phase transition of adsorbed layer**

Figure S5: $I\,[v_{as}(CH_2)]\,/\,I\,[v_s(CH_2)]$ ratios at equilibrium at various temperatures. This implies, at equilibrium, the phase transition of DDAO adsorbates at the interface is similar to a melting process, in which the $I\,[v_{as}(CH_2)]\,/\,I\,[v_s(CH_2)]$ ratios decrease when temperature increases.

3

References

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