Supporting Information for:

ADSORPTION OF QUANTUM DOTS ONTO POLYMER AND GEMINI SURFACTANT FILMS: A QUARTZ CRYSTAL MICROBALANCE STUDY

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1. **Analysis of the rheological properties of PMAO films**.

In this section, we present a brief outline of the Voigt' model used to interpret the Δf and ΔD experimental data corresponding to the polymer PMAO The model describes viscoelastic behavior on the basis of two components, the elastic component interpreted as a spring and the viscous contribution interpreted as a dashpot. Accordingly, the viscoelastic adlayer is characterized by the complex shear modulus, G*, as follows:

$$\mathbf{G^* = G' + iG''} = \mu_1 + \mathbf{i}\, 2\pi \mathbf{f}\, \eta_1 \qquad [1]$$

Where G' and, G'' represent storage and the loss modulus, respectively. μ_1 is the elastic shear modulus, f is the oscillation frequency and η_1 is the shear viscosity. The model describes the propagation of the damping of shear bulk acoustic waves in a homogenous viscoelastic adlayer in contact with a bulk Newtonian fluid under no-slip conditions [1, 2]. The adlayer [3]parameters involved in the model are, the adlayer density (d) and thickness (h) and the elastic shear modulus (μ_1) and viscosity (η_1).

The Δf and ΔD experimental data are related to the adlayer parameters by the following equations[1]:

$$\Delta f \approx -\frac{1}{2\pi\rho_0\, h_0}\left\{\frac{\eta_2}{\delta_2} + h_1\rho_1\,\omega - 2h_1\left(\frac{\eta_2}{\delta_2}\right)^2 \frac{\eta_1\omega^2}{\mu_1^2+\omega^2\eta_1^2}\right\} \qquad [2]$$

$$\Delta D \approx -\frac{1}{\pi f\rho_0\, h_0}\left\{\frac{\eta_2}{\delta_2} + 2h_1\left(\frac{\eta_2}{\delta_2}\right)^2 \frac{\eta_1\omega}{\mu_1^2+\omega^2\eta_1^2}\right\} \qquad [3]$$

In eq. 2 and 3 ρ_0 y h_0 represent the density and thickness values of the crystal, respectively. η_2 and ρ_2 are the viscosity and density values of the liquid, chloroform in our system, and ω represents the angular frequency, $\omega = 2\pi f$. δ_2 represents the viscous penetration depth of the liquid, expressed as: $\delta_2 = \sqrt{\frac{2\eta_2}{\omega\rho_2}}$

Experimental data of Δf and ΔD corresponding to the 3,5,7,9 and 11 overtones were employed to obtain the best fitting values of the adlayer parameters by means the Q-Tools software (Q-sense, Sweden). The density and viscosity values of chloroform were provided by the manufacturer, 1480 kg m^{-3} and 0.000563 Pa s, respectively. The density of the adlayer is usually considered as the average between the solvent and coating molecules densities[4, 5]. Using this criterion the density values for the polymer adlayer was 1300 kg m^{-3}. Finally, the boundary conditions used for the fit procedure were: viscosity from $1x10^{-5}$ to 0.1 Pa s; the shear modulus from 10 to $1x10^{8}$ Pa and the surface mass from 30 to $1x10^{5}$ ng cm^{-2}.

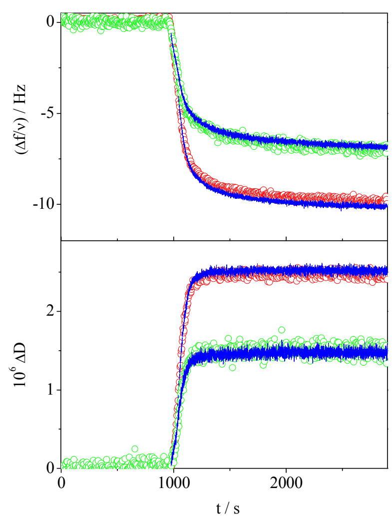

Figure 1s Experimental $\Delta f/\nu$ and ΔD data for the PMAO film ($1x10^{-2}$M) for two frequency overtones: 3rd (–) and 9th (–). The blue lines show the fit with the Voigt model.

2. Kinetics of adsorption of coatings and QDs

Illustrative examples of adsorption curves of the polymer PMAO and the Gemini surfactant 18-2-18 are presented in Figure 2s. The adsorption curves do not follow an exponential law, see Figure 3s, and can be interpreted as the sum of two exponential functions by:

$$\Gamma(t) = \Gamma - A_1 \exp(-t/\tau_1) - A_2 \exp(-t/\tau_2) \qquad [4]$$

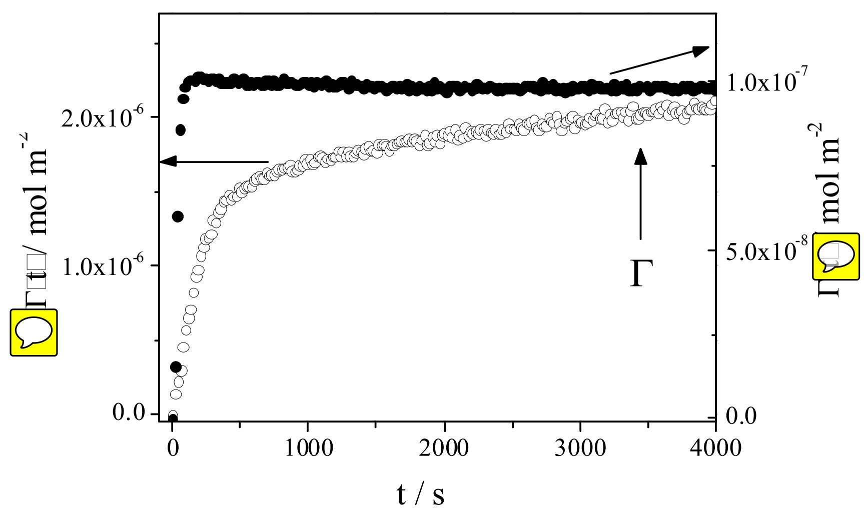

Figure 2s. Representative adsorption curves, Γ vs. time, for: PMAO (solid symbols) and Gemini surfactant (open symbols) molecules

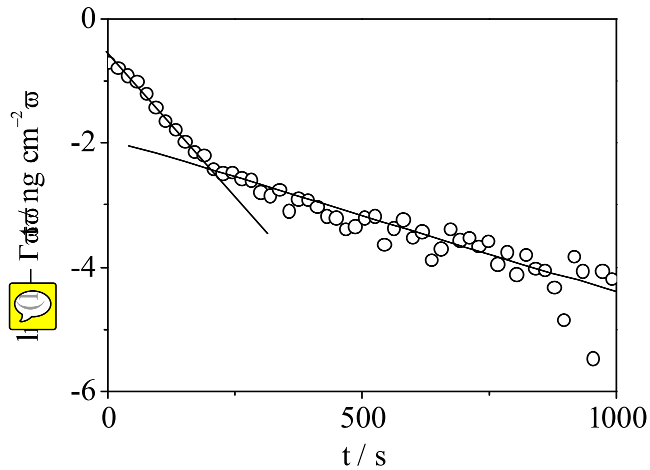

Figure 3s. Representative example of the adsorption curve represented in terms of eq.4 for PMAO 1×10^{-2} M.

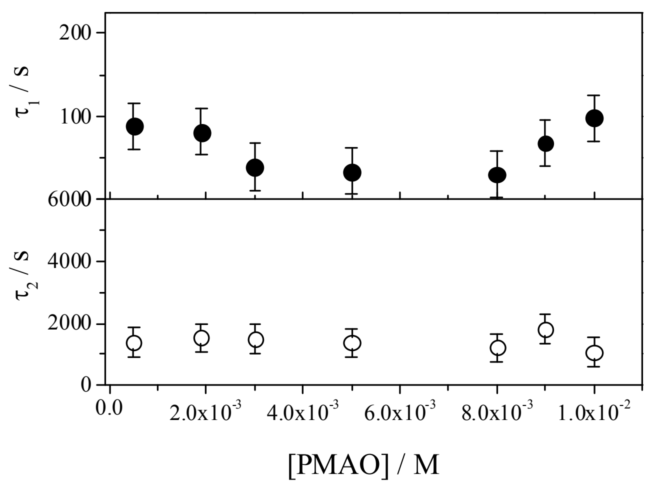

Figure 4s. Variation of the relaxation times values with the polymer concentration introduced in the cell

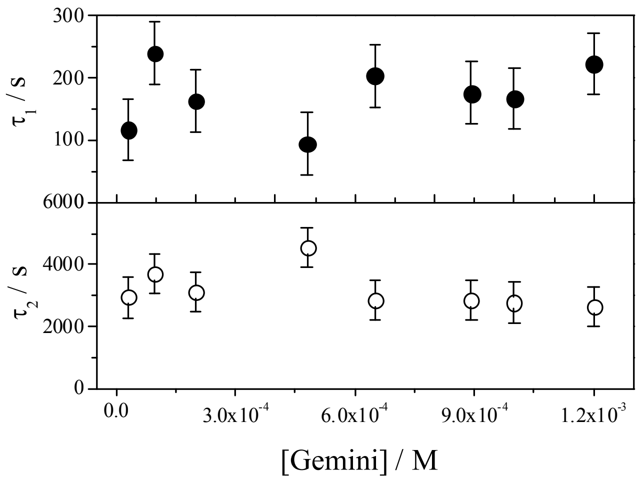

Figure 5s. Variation of the relaxation times values with the surfactant concentration introduced in the cell.

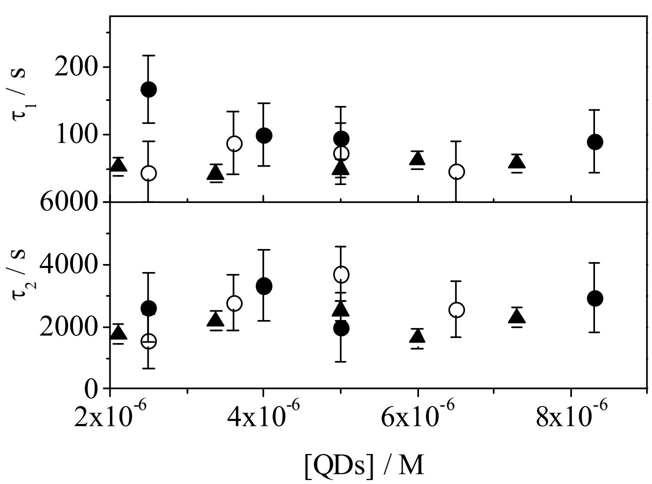

Figure 6s. Variation of the relaxation times values with the QDs concentration introduced in the cell.

References

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