

## Effects of Bulk Aggregation on PEI/SDS Monolayers at the Dynamic Air/Liquid Interface: Depletion due to Precipitation versus Enrichment by a Convection/Spreading Mechanism

*Anna Angus-Smyth<sup>1,2\*</sup>, Colin D. Bain<sup>2</sup>, Imre Varga<sup>3</sup> and Richard A. Campbell<sup>1\*</sup>*

1. Institut Laue-Langevin, 6 rue Jules Horowitz, BP 156, 38042 Grenoble Cedex 9, France

2. Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, United Kingdom

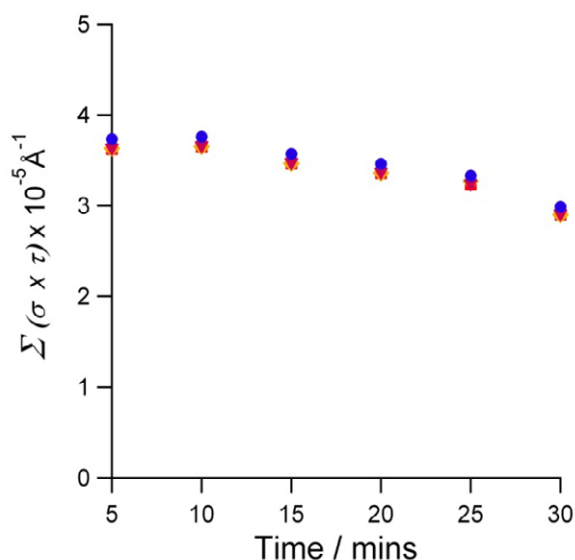
3. Institute of Chemistry, Eötvös Loránd University, Budapest 112, P. O. Box 32, H-1518 Hungary

\* Corresponding author. E-mail: [campbell@ill.eu](mailto:campbell@ill.eu). Phone: +33476207097 or

Email [annaangussmyth@gmail.com](mailto:annaangussmyth@gmail.com) Phone +441793442572

### Electronic Supporting Information

#### 1. Effect of the Model Used in Fitting the NR data



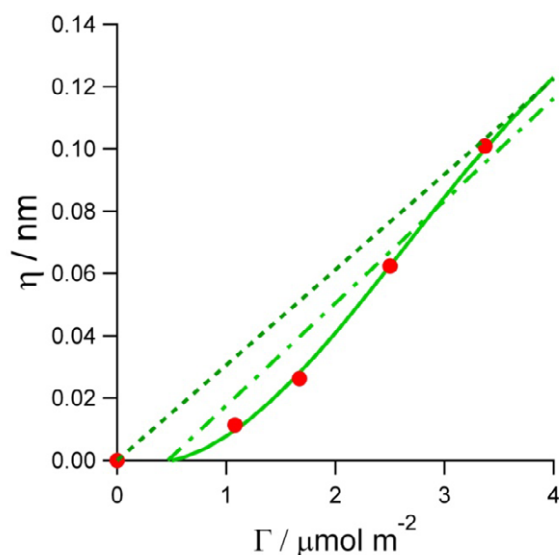
**S.I. Fig. 1.** Effect of the structural model used in fitting the NR data on the value of  $\sum_i(\sigma_i \times \tau_i)$  obtained. The data shown here were all measured on PEI/SDS at pH 10 for which the co-modelling methodology was applied, where the concentration of SDS

was 0.32 mM (purple triangles in Figure 1 (a) in the main text), of PEI was 100 ppm, and of NaCl was 0.1 M. The different structural models used were a 11-Å layer (red squares) a 20-Å layer (purple triangles), a 50-Å layer (blue circles) and two layers where the top layer was 11-Å and the sub layer 20-Å (yellow diamonds).

In our previous work on polymer/surfactant mixtures we demonstrated that the value of  $\sum_i(\sigma_i \times \tau_i)$  obtained from fitting specular neutron reflectivity profiles was minimally dependent on the structural model used.<sup>1</sup> As a consequence, the effect of the structural model on the calculated interfacial composition was also minimal. S.I. Fig.1. demonstrates that the same is true for PEI/SDS pH 10, as the value of  $\sum_i(\sigma_i \times \tau_i)$  is affected only by  $\sim 3\%$  of the maximum value by the choice of structural model. Therefore a single layer model with an 11 Å thickness was used in fitting the NR data.

## 2. Co-Modelling Methodology

As a consequence of there being only a small deviation in the linearity of the  $\eta(\Gamma)$  calibration for the pure surfactant, the contribution of surfactant to  $\eta$  for the mixture can be approximated by either a linear or a cubic function, each of which was used in our co-modelling approach for PEO/surfactant mixtures for different reasons.<sup>1</sup> In order to determine the most appropriate function to account for the contribution of surfactant to  $\eta$  for a given polymer/surfactant system, we can calculate the interfacial composition using various approaches.

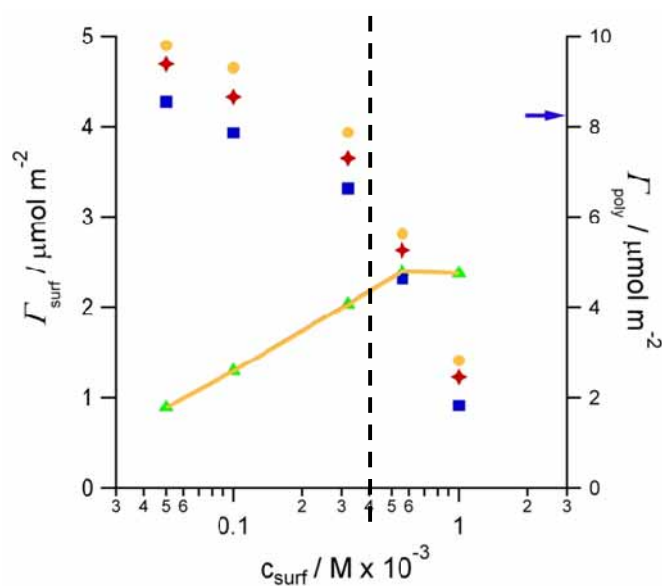


**S.I. Fig. 2.** Plot of the ellipsometric thickness,  $\eta$ , of pure SDS solutions against the surface excess,  $\Gamma$ . The different lines are different functions to fit the data, where the solid line is a cubic fit to the data, the dash-dot line is a linear fit to the data, and the dashed line joins the minimum and maximum values.

In this study, the contribution of the surfactant to ellipsometry data is approximated by a single coefficient,  $C$  (see eq. 10 in the main text).  $C$  is obtained from the gradient of a line through the points  $\eta = 0$ ,  $\Gamma = 0$  and the values of the same quantities for a monolayer of pure surfactant. In our previous study,<sup>1</sup> the contribution of surfactant was approximated by a linear or cubic function fitted through all of the pure surfactant data. These three functions for the pure surfactant data are shown in S.I. Fig. 2.

From S.I. Fig. 2 it is clear that a cubic function gives the best fit to the pure surfactant  $\eta$  v  $\Gamma$  data, whilst a straight line over-estimates  $\eta$  at low  $\Gamma$  values, and a line joining the minimum and maximum values over-estimates  $\eta$  at all values of  $\Gamma$ . A cubic function is necessary to approximate the data for the pure surfactant due to the non-linearity of the relationship at low coverage as the surfactant is mixed with air and water.<sup>2</sup> However, for a polymer/surfactant mixture if a high amount of polymer adsorbs at low surfactant coverage, as it does for PEI/SDS at pH 10 (see S.I. Fig. 3 below or Figure 2 in the main text), the need for a cubic fit will be eliminated because changes in the surfactant conformation would not be expected. Therefore the relationship between  $\eta$  and  $\Gamma$  in the mixture can reasonably be approximated as linear. Use of a linear function through the pure surfactant data (dash dot line in S.I. Fig.) will result in an offset at low coverages; as the line does not go through the origin a surfactant surface excess of zero cannot be achieved, which is a physical impossibility. As a consequence of this we decided that the best approximation to the surfactant contribution for the mixture is given by the dashed line, resulting in the single co-efficient  $C$ .

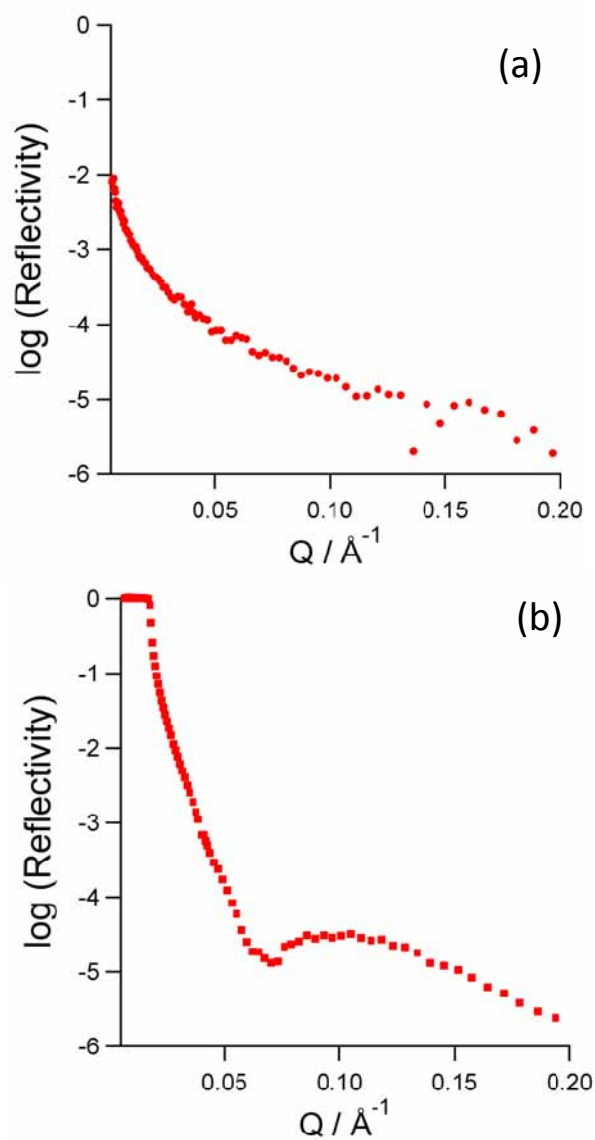
S.I. Fig. 3. shows the effect of the choice of function used to approximate the contribution of the surfactant to  $\eta$  for the mixture on the calculated composition (similar to Figure 2 in the main text). From these data it is clear that both of the functions resulting from fits to the pure surfactant data result in an over-estimation of the polymer coverage at low  $c_{\text{surf}}$  values, to the extent that  $\Gamma_{\text{poly}}$  exceeds the maximum possible value which can be reached by diffusion controlled adsorption of polymer/surfactant complexes (which is marked by the blue arrow on the right hand axis). The function used has a minimal effect on the surfactant coverage however. The differences between the surfactant surface excesses in S.I. Fig. 3. demonstrate the error which would be incurred in our methodology by use of an inappropriate function to calibrate the contribution of the surfactant to  $\eta$  for the mixture.



**S.I. Fig. 3.** Interfacial composition calculated using fitted values of  $\sigma \times \tau$  from NR data and  $\eta$  from ellipsometry data using the three different functions shown in S.I. Fig. 2 to account for the contribution of surfactant to  $\eta$  for the mixture. The green triangles and blue squares are the data calculated using a single co-efficient (as in Figure 2 in the main text), whilst the yellow circles and yellow line shown the polymer and surfactant excesses calculated using the cubic function, and the red diamonds and red line (not resolvable from the yellow line) show the surface excesses calculated using the linear fit to the pure surfactant data. It should be noted that the coloured lines do not have the same meaning as the dashed lines in Figure 2 in the main text, here they are used to denote the data points for the surfactant in the mixture. The vertical dashed line shows the point at which bulk phase separation occurs, as in Figure 2 in the main text.

### 3. Neutron Reflectivity Data for PEI/SDS at pH 10

Previous studies of solutions of PEI/SDS solutions at pH 10 at the static air/water interface have demonstrated large surface excesses, attributed to interfacial multilayers for 2k and 25k polymers from NR data<sup>3,4</sup> and embedded aggregates for 750k polymer using ellipsometry.<sup>5</sup> On the OFC, none of our NR data recorded using 750k PEI/SDS mixtures in the specular reflectivity profiles exhibited a Bragg peak indicative of interfacial multilayers, and an example of such data is shown in S.I. Fig. 4(a). To resolve whether this observation may be attributed to the polymer molecular weight or to the expansion of the interface was expanding on a sub-second time scale, static data recorded on FIGARO's adsorption troughs, such as that shown in S.I. Fig. 4 (b), were also recorded. The static data also do not exhibit a Bragg peak indicative of interfacial multilayers.



**S.I. Fig. 4.** Specular neutron reflectivity profiles recorded on PEI/SDS at pH 10 at both the dynamic and static air/water interfaces. (a) is data recorded on the OFC where the bulk concentration of SDS is 0.56 mM and the isotopic contrast is h-polymer/d-surfactant/NRW, and (b) is data recorded at the static interface where the bulk concentration of SDS is 0.66 mM and the isotopic contrast is h-polymer/h-surfactant/D<sub>2</sub>O.

#### 4. Comparison of our maximum values of $\eta$ to the values of $\delta\Delta$ measured by Tonigold et al.

In order to compare our data to those of Tonigold et al,<sup>5</sup> it was necessary to convert their ellipsometric values of  $\delta\Delta$  to  $\eta$ . This can be effected using the following relationships,<sup>6</sup>

$$\delta\Delta = g(\varphi) \frac{\eta}{\lambda}$$

Where  $g(\varphi)$  is a function which depends only on the bulk properties (the refractive indices of air, 1, and water, 1.33) and the angle of incidence of the ellipsometry measurements  $\varphi = 53.1^\circ$

$$g(\varphi) = \frac{4\pi n_{\text{air}} n_{\text{soln}}^2 \cos\varphi \sin^2\varphi}{(n_{\text{soln}}^2 - n_{\text{air}}^2)[(n_{\text{soln}}^2 + n_{\text{air}}^2)\cos^2\varphi - n_{\text{air}}^2]}$$

Tonigold et al measured a phase shift of  $3^\circ$  for a polymer/surfactant monolayer in the absence of aggregates at the surface, which corresponds to an ellipsometric thickness of  $\eta \approx 0.3 \text{ nm}$ .<sup>5</sup>

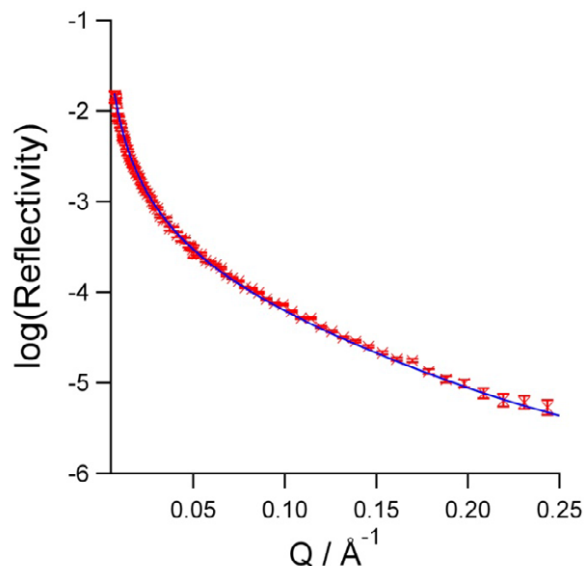
#### 5. Details of Simulation of the Ellipsometric Response to PEI/SDS Aggregates at the Surface

The optical simulation of the response of  $\eta$  to the presence of a layer of PEI/SDS aggregates at the air/water interface, which is shown in Figure 7 in the main text, was performed using Film Wizard software,<sup>7</sup> an optical matrix model of stratified interfaces. The simulation was performed for measurements at the Brewster angle of pure water ( $53.08^\circ$ ) and the wavelength of a HeNe laser (632.8 nm).

PEI/SDS aggregates have been shown by Bastardo et al to be lamellar with a d-spacing of  $37 \text{ \AA}$ .<sup>8</sup> To calculate the refractive index of the aggregates we need an estimation of the bilayer thickness in the lamellae. We can estimate this thickness from a measurement of the thickness of an SDS monolayer at saturation coverage. The SDS data in S.I. Fig. 5 converge to a layer thickness of  $11 \text{ \AA}$ . Although previous studies have used thicker layers of around  $18 \text{ \AA}$ ,<sup>9</sup> such a layer structure was not compatible with our experimental data.

The thickness of the SDS bilayers in the lamellae may then be taken as  $22 \text{ \AA}$ . The volume fraction of SDS in the aggregates,  $\Phi_{\text{SDS}}$ , is therefore 0.595. From the molar volume of SDS,  $V_m = 403 \text{ \AA}^3$ <sup>10,11</sup>, and  $N_A$ , we can therefore work out the number of moles of SDS per  $\text{m}^3$ ,  $2451 \text{ mol m}^{-3}$ . At pH 4, 67% of the PEI monomers will be associated with an SDS molecule, therefore in the aggregates we can assume that there are 1.5 PEI monomers per SDS molecule, giving us a value of the moles of PEO per  $\text{m}^3$ ,  $3676 \text{ mol m}^{-3}$ . Using the molecular weight of a PEI monomer (43) and the density of PEI,  $\rho_{\text{PEI}} = 0.9974 \text{ g cm}^{-3}$ <sup>12</sup>, we can

therefore calculate a volume fraction of PEI in the aggregate,  $\Phi_{PEI} = 0.159$ . The volume fraction of water  $\Phi_{H_2O}$  is then 0.246.



**S.I. Fig. 5.** Specular neutron reflectivity profile of 1.25 mM SDS in the presence of 0.1 M NaCl recorded on the OFC in the isotopic contrast d-surfactant/NRW recorded as part of this project. The blue fit shown is using a single 11-Å layer structure.

From the volume fractions of the three components in the aggregates, and the refractive indices of the species, the refractive index of the aggregates can be calculated. The refractive indices of water and PEI were obtained from the literature,  $n_{H_2O} = 1.331$  and  $n_{PEI} = 1.52$ .<sup>13, 14</sup> The refractive index of SDS was calculated from values of the refractive index increment,  $dn/dc_{SDS} = 0.1195$ ,<sup>15</sup> and the density of SDS,  $\rho_{SDS}$ , calculated from  $V_m = 403 \text{ \AA}^3$ <sup>10, 11</sup> =  $0.1094 \text{ g cm}^{-3}$ .  $n_{SDS}$  is then given by

$$n_{SDS} = n_{H_2O} + \left( \frac{dn}{dc_{SDS}} \times \rho_{SDS} \right) = 1.462$$

The refractive index of the aggregates can then be calculated from

$$n_{agg} = (\Phi_{SDS} \times n_{SDS}) + (\Phi_{PEI} \times n_{PEI}) + (\Phi_{H_2O} \times n_{H_2O}) = 1.44$$

$n_{agg}$  can then be used to simulate the effect of the layer thickness,  $d$ , on the ellipsometric thickness,  $\eta$ , resulting in Figure 6 in the main text. We note that in spite of the assumptions in the calculations of the refractive index of PEI/SDS aggregates above, the conclusion reached from both the optical simulation in Figure 8 of the main text is clear: fluctuations in the ellipsometry data cannot originate from polydisperse aggregates adsorbing intact to the air/water interface, as both positive and negative spikes in  $\eta$  would

result. Even if the calculated refractive index of the aggregates was elsewhere in the range 1.4–1.5 the conclusions would be unaffected.

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