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# Surfactants at the Solid-Liquid Interface: Measurements at higher concentrations using Optical Reflectometry

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## Abstract

Both adsorbing and non-adsorbing surfactant solutions have been investigated by optical reflectivity (OR) on a hydrophilic silica surface over a wide range of solution concentrations. The use of the OR technique is tested at surfactant concentrations well above those usually employed with this approach. To establish a correlation with the OR response expected from these solutions, a simple additive two-part model is introduced comprising an interfacial term and a bulk solution term. The adsorbing system demonstrated the expected regular adsorption isotherm behaviour at lower solution concentrations, and at higher solution concentrations more closely fitted the bulk solution response. When this bulk response was subtracted from the total OR signal, a constant adsorbed amount was found, validating our two-part model approach. Whilst data obtained from alcohol-water mixtures also showed the expected non-adsorbing system response with the signal arising exclusively from the bulk solution, other systems (sucrose solutions and non-adsorbing sodium dodecylsulphate) showed more complex behaviour even after the solution refractive index changes had been subtracted. The implications of these data for probing depletion effects for these systems are discussed.

**Keywords:** Optical reflectometry, surfactants, sucrose, CTAB, SDS

## 1. Introduction

Surfactant and polymer adsorption at the solid-liquid interface is of critical interest to an extremely wide range of colloidal systems across a wide range of processes and formulated products. [1-4] Knowledge about features such as the adsorbed amount and the adsorption kinetics across a range of relevant conditions has obvious value for the design and iterative improvement of these products and processes. As a result, considerable effort has been expended to develop measurement technology capable of providing accurate adsorption data. [1] One outstanding challenge is to obtain such information for relatively concentrated solutions of these polymer and/or surfactant systems.

The development of optical reflectometry as a route to study the kinetics of polymers, particles and surfactants adsorption at the solid-solution interface has been widely reported over the last 20 years. [5-7] Careful utilization of impinging jet hydrodynamics with an associated stagnant point has allowed free diffusion measurements of adsorption kinetics to be achieved. The use of this approach has been validated in a number of systems and the data have highlighted a range of previously unreported adsorption features such as the direct role of micelles in the adsorption process above the critical micelle concentration (cmc). [8,9] Another example is the anomalously long adsorption seen for simple surfactants, such as cetyltriimethylammonium bromide (CTAB) at the silica-solution interface just below the cmc. [8] Similar measurements of adsorption have now been reported for a wider range of surfactants across a variety of surfaces. Other comparable data have also been reported for surfactants using evanescent wave Raman scattering with comparable stagnation point flow. [10]

Despite the obvious appeal of this instrument for the study of surfactant adsorption at solid-liquid interfaces, all reports in the literature to date are limited to concentrations up to, or just above, the cmc. Whilst this region is clearly of interest there are many practical applications where access to data from a much wider range of concentrations, especially well above the cmc will have value. For example, shampoo and conditioner formulations will frequently operate at much higher concentrations. It has been previously observed that at higher concentrations of surfactant or polymer, anomalous changes in the measured signals from optical reflectometry make analysis using the standard four-layer model (see methods section below) problematic and, as a result, this region has not been explored further. [8, 9, 11, 12]

In this paper, we measure some simple test systems across a much wider range of concentrations than has been previously reported to explore further the utility of this measurement approach for these types of systems. Importantly, we explore routes to allow analysis of the data at much higher bulk concentrations such that meaningful analysis of the adsorbed surfactant can be made in these concentration regions. We also further explore the utility of this approach by examining both adsorbing and non-adsorbing systems at the solid-liquid interface.

## 2. Methods and Materials

### *2.1 Optical Reflectometry Theory*

The optical reflectometer (OR) typically measures the ratio of the polarized reflected laser light, S: The most common definition of S is $S = f(R_p/R_S)$, for reflection coefficients in the parallel and perpendicular polarizations $R_P$ and $R_S$, respectively. For any particular experimental setup f may be found using f = $S_0/(R_p/R_S)_0$, i.e. from the initial values of $R_P$ and $R_S$ at the beginning of the experiment, so that f is a constant thereafter. In terms of the reflected intensities, we may use $\Delta S = \frac{I_P}{I_S} - \frac{I_P^0}{I_S^0}$ = S – $S_0$, where the superscript 0 indicates the initial values. Since the reflectometer angle of incidence is usually set near to the Brewster angle, $I_P$ will at first increase and $I_S$ will decrease slowly [5], meaning that S will initially be larger than $S_0$ resulting in a positive value for ΔS.

If the phase shift, ϕ, of the laser beam after it emerges from the OR cell becomes large enough so that $R_P$ and $R_S$ (and hence $I_P$ and $I_S$) begin to change in the opposite sense, then $I_p/I_S$ will begin to decrease until it becomes similar to and then smaller than $I_P^0 / I_S^0$ [5]. When this occurs, ΔS is then negative.

The standard way of modeling OR data is to treat the system as a simple set of homogenous slabs as shown in Figure 1.

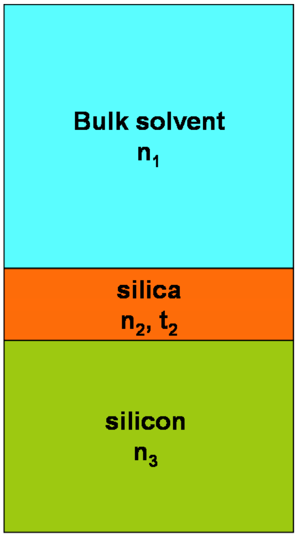

**Figure 1:** A typical 3-layer model used for reflectivity data. The refractive indices are labeled as $n_1$, $n_2$ and $n_3$ for the bulk solvent, silica and silicon respectively. The thickness of the silica layer is labeled as $t_2$. The thickness of the other 2 layers is assumed to be infinite.

A couple of important points arise from this simple model: (a) the properties of the layers are constant and continuous up to a line separating each layer, and (b) the thickness of layer 2 (silica) is the main variable. The consequence of (b) is that for any particular instrument setup (laser angle, silica thickness etc.) the model will output the same data file each time. One experimental test for the OR setup is to use alcohol-water mixtures [14] as shown in Figure 2.

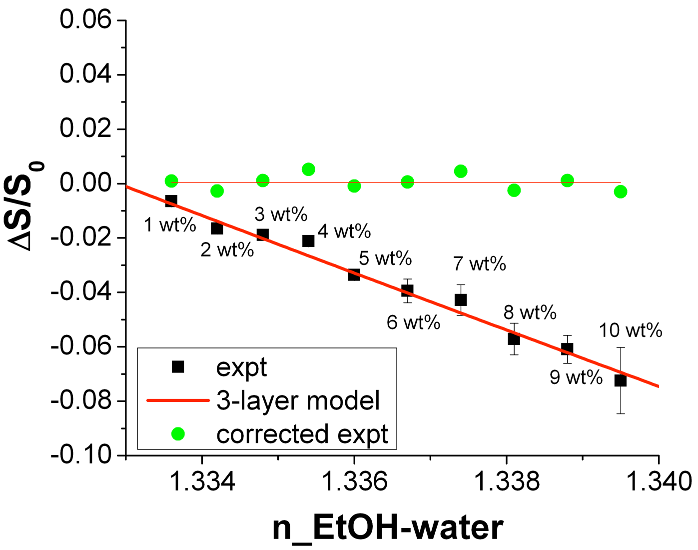

**Figure 2:** OR data for ethanol-water mixtures showing the percentage of EtOH used. Raw data (black squares) are plotted alongside the 3-layer model (red line) and the bulk corrected data (green circles). A line has been placed through the corrected data to guide the eye.

The raw OR data in Figure 2 show a linear response of the OR as the ethanol concentration is increased. The 3-layer model represents changes in the bulk refractive index of the mixture and fits the experimental data nicely over a wide range of EtOH concentrations. When the 3-layer model fit is subtracted from the OR data (green circles in Figure 2) the residual corrected data points (green) show that all the deviation from a zero value of $\Delta S/S_0$ in this case arises exclusively from the bulk refractive index changes of the ethanol-water solution. This is good confirmation that our device is working correctly with no material unknowns for the silica/silicon substrate.

For an adsorbing system an extra layer is needed in the model between the bulk solution and the silica layer to create a four-layer model. [6] For these adsorbing systems it is possible to consider the OR signal to be made up of two components:

$$\frac{\Delta S}{S_0} = A\left(\frac{\Delta S}{S_0}\right)_i + B\left(\frac{\Delta S}{S_0}\right)_b \qquad (1)$$

Where A and B are sensitivity coefficients at the silica-solution interface (i) or of the bulk solution (b), respectively.

Usually, the OR is setup such that the first term (the interfacial term) is much larger than the second (bulk) term. However, as the bulk solution concentration increases, the second term gradually becomes more important. The interfacial term depends critically on how much material is able to adsorb at a surface, its optical properties, and instrument parameters such as the angle of incidence. For any particular instrument setup the value of A should be a constant [15] and a change in $\left(\frac{\Delta S}{S_0}\right)_i$ will be found that may be represented by a surface adsorption isotherm.

In this simple model, the adsorption at the interface is assumed to be independent of the bulk solution, as commonly assumed in slab-type models. At some point, it is common for the adsorption isotherm to show a maximum value and at this point, a maximum value for $\left(\frac{\Delta S}{S_0}\right)_i$ is also found. Further increases in the bulk concentration of adsorbate will change only the magnitude of $\left(\frac{\Delta S}{S_0}\right)_b$ and this may then become significant.

Our two-part model assumes that a bulk solution term can be treated as a simple addition to the surface adsorption term. The consequences of this approach and possible limitations will be explored below using well-defined experimental systems.

### *2.2 Materials*

HPLC grade ethanol was obtained from Fischer. Cetyltrimethylammonium bromide (CTAB), sodium dodecylsulphate (SDS) and sucrose were purchased from Sigma-Aldrich. The water used was MilliQ ultra-pure water of mean resistivity 18 MΩcm.

The optical reflectometer (OR) was purchased from the University of Wageningen and uses a 1 mW red He-Ne laser at 632.8 nm, positioned so that the incident angle onto the sample surface in water was 68.5 °. The entire OR rests inside an incubator at a constant 25.0 ± 0.1 °C. Liquid flow is gravitationally controlled into the OR cell at a flow rate of 3 ml/min. Exchange between the solvent and solution under test is carried out via a simple two-way valve. The method of use for the OR has been described previously [16]. 76 mm diameter silicon wafers were purchased from Silicon Valley Microelectronics Inc., USA. A thermal oxide coating of 115 nm had been deposited onto the top side of the wafers by the manufacturer. These wafers are extremely smooth and have a typical roughness (peak to trough) of 0.65 nm, as determined from a 1 x 1 $\mu$m AFM scan of the surface. The wafers were cut into strips approximately 1 cm wide and treated by placing them into an ultra-violet light cleaner (Bioforce Nanosciences Inc.) for 1 hour prior to rinsing with MilliQ water and then inserted into the OR cell. This process rendered the silica surface to be very hydrophilic.

## 3. Results and discussion

### 3.1 Adsorbing solutions

Experimental OR adsorption data for CTAB in water on silica over a wide range of concentrations are presented in Figure 3. CTAB has been reported in a number of papers previously, [8, 11-13] and as such provides a good baseline against which to test our measurement technique and analysis approach.

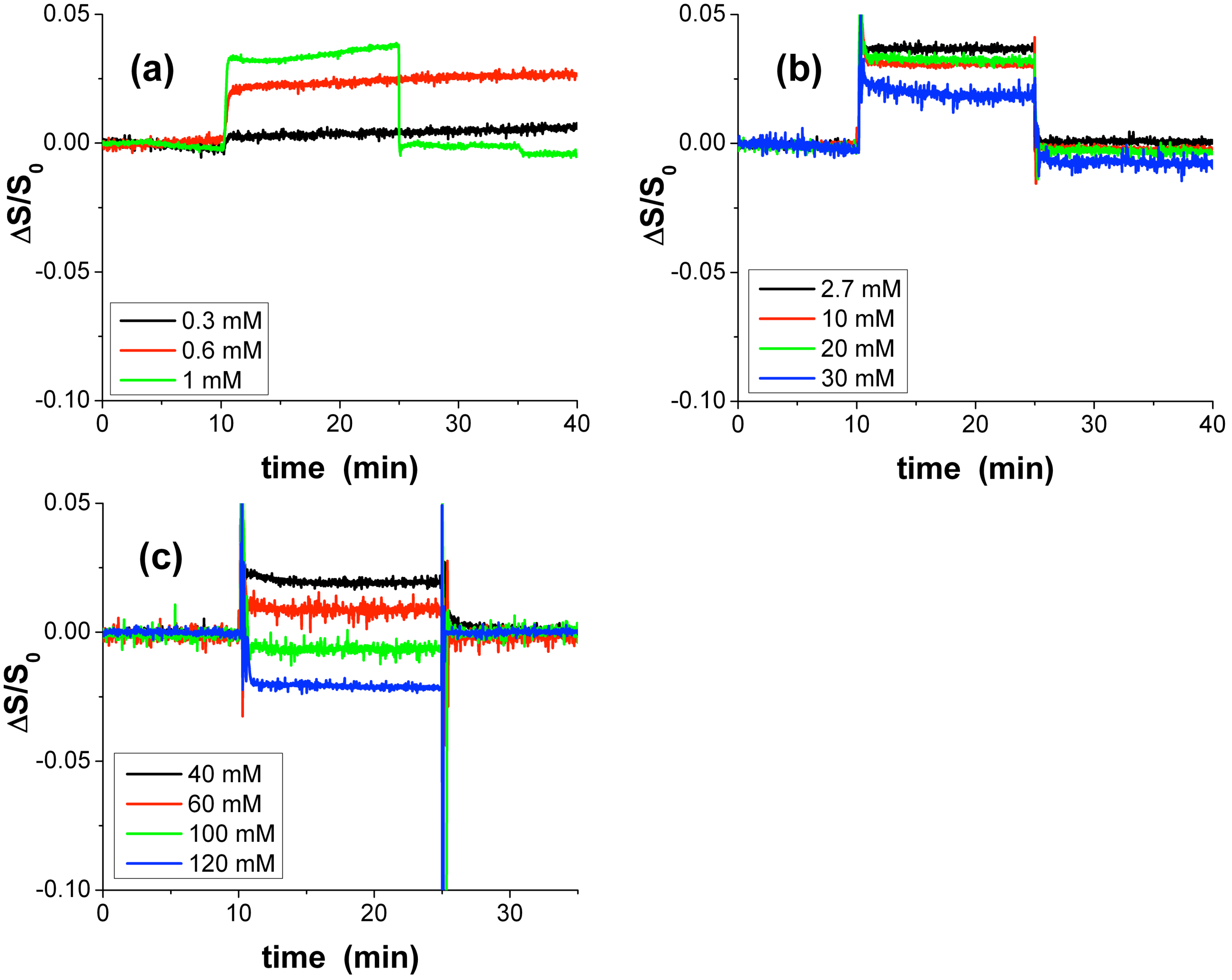

**Figure 3:** Adsorption experiments with CTAB in water onto silica by OR, (a) at concentrations upto the CTAB cmc, (b) medium concentrations above the cmc, (c) at high concentrations.

Figure 3 shows the experimental data acquired for the adsorption of CTAB at the silica-solution interface. In all cases, CTAB solutions are introduced after a 10 minute background stability measurement in water. After 25 minutes, water was introduced into the OR cell to rinse off the CTAB. The rinse off data for 0.3 mM and 0.6 mM CTAB are not shown here, as a longer time was required for adsorption to equilibrium at these low concentrations. The kinetics of these systems has been investigated previously and it was shown that different interfacial structures lead to different kinetics [8, 17]. At concentrations upto the CTAB cmc, Fig. 3(a), the adsorption is relatively slow and only gradually reaches a plateau [8], with this plateau value increasing according to the well-known S-shaped adsorption isotherm [8,17]. However, if the CTAB concentration is increased to values above the cmc, Fig. 3(b), the adsorption profile achieves a stable value as before, but the magnitude of the shift in $\Delta S/S_0$ after initially remaining constant (10 and 20 mM) begins decreasing as a function of increased concentration (> 30 mM). This trend continues at higher CTAB concentrations, Fig. 3(c), and the plateau value of $\Delta S/S_0$ eventually becomes negative. Note that at each concentration the introduction of water into the OR cell (at 30 mins) rapidly returns $\Delta S/S_0$ to zero (the 0.3 and 0.6 mM data require longer than shown for a stable value to be obtained before rinsing [8]).

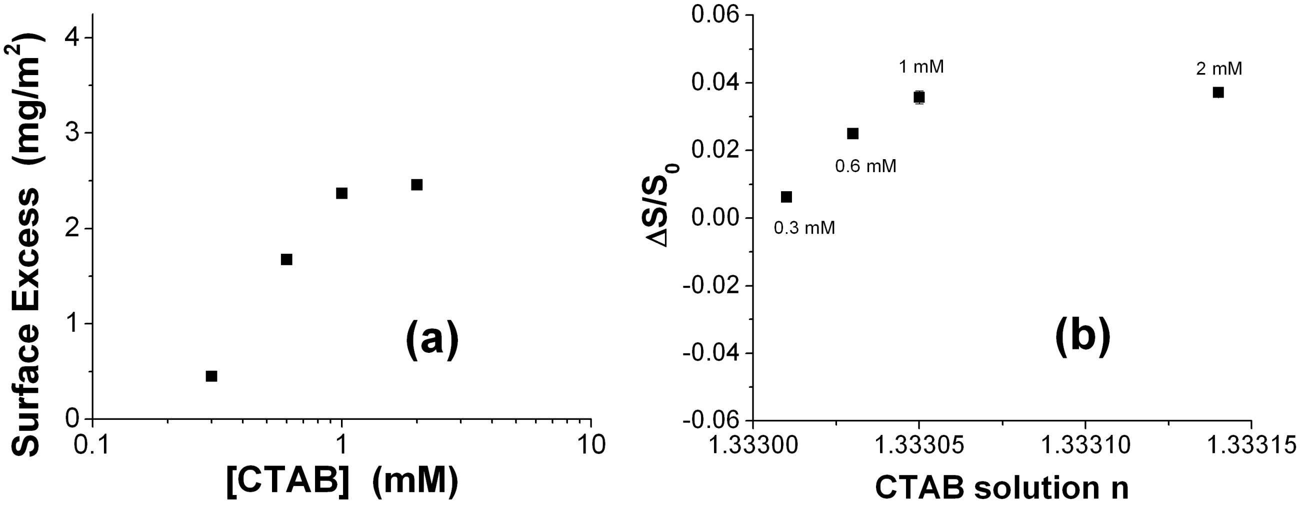

**Figure 4:** The adsorption behaviour of CTAB on hydrophilic silica from water at low concentrations (a) plotted as an isotherm and (b) the same data plotted as changes in $\Delta S/S_0$ versus the solution refractive index [9].

Figure 4(a) demonstrates that when the refractive index of the bulk solution is low the recorded changes in $\Delta S/S_0$ correspond to the published adsorption isotherm behaviour [8]. These data show that at low concentrations there is a close relationship between the amount of adsorbed surfactant and the measured OR signal, $\Delta S$. Any changes in the bulk solution refractive index do not, therefore, significantly affect the OR measurement under these conditions.

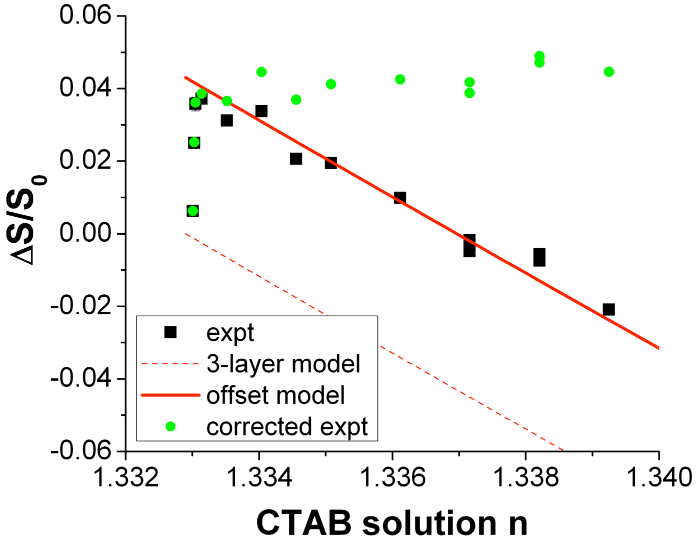

**Figure 5.** OR data for CTAB over a wide range of concentrations. The experimental data (black squares) are shown alongside the 3-layer model (dashed red line), the offset 3-layer model (solid red line) and the bulk corrected experimental data (green circles).

Figure 5 shows the entire data set obtained for CTAB upto 120 mM. When the bulk CTAB concentration is around 30 mM, i.e. significantly above the cmc (0.9 mM), $\Delta S/S_0$ begins to decrease. It is at these higher solution concentrations that the OR signal becomes dominated by the bulk refractive index changes. To demonstrate this bulk effect, the 3-layer model described earlier has been plotted alongside the measured data in Figure 5 (dashed red line). This model lies well below the data due to the presence of the adsorbed layer of CTAB, which is not included in the model. Our simple two-part description of the behaviour of the OR, equation (1), allows that we should add an offset to the 3-layer model to account for the adsorbed layer of CTAB. Figure 5 shows that once this offset has been applied to the 3-layer model (solid red line), both the model and the measured data overlap each other. It we then subtract the bulk solution refractive index effect from the $\Delta S/S_0$ values then the green data points in Figure 5 are the result. This shows that the adsorbed amount of CTAB is approximately uniform upto concentrations many times that of the cmc. Although this conclusion is perhaps not surprising, it is a good indication of the validity of our approach.

### 3.2 Non-adsorbing solutions

We have shown that when an adsorbing material (CTAB) is introduced into the OR at high enough bulk concentrations, the overall response of the OR is eventually dominated by the changes in the bulk refractive index of the CTAB solution. When a non-adsorbing material is introduced into the OR, only the bulk solution behaviour is expected to be seen, see for example the ethanol-water data in Figure 2.

Sucrose is an ideal material to further test our OR measurement and analysis approach as its optical properties are well known [18] and it is soluble in water to very high bulk concentrations.

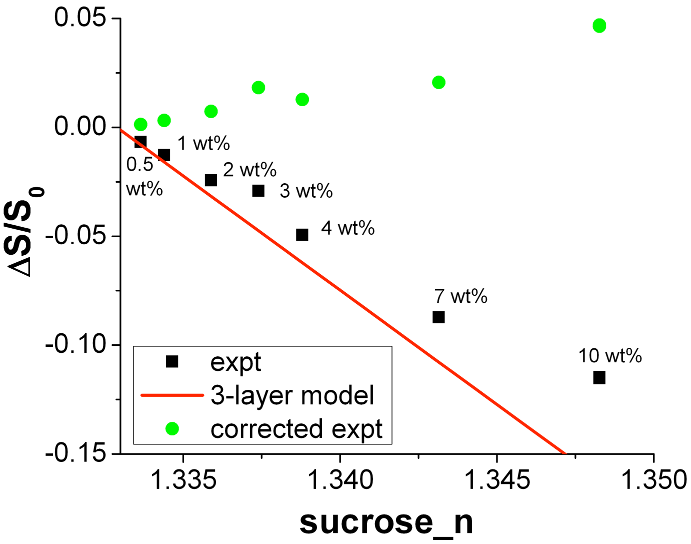

**Figure 6:** The response of the OR to sucrose solutions for a hydrophilic silica substrate. Shown are the raw experimental data (black squares), the 3-layer model for changes in the bulk solution refractive index (red line) and the experimental data after correction for the bulk refractive index (green circles).

Most of the raw OR data shown for sucrose in Figure 6 (black squares) do not lie over the predicted bulk behaviour from the simple 3-layer model. According to our two-part description of the OR response, equation (1), assuming no adsorbed layer exists for sucrose, then the first part of equation (1) should be zero. The only response expected from the description is then due to the bulk liquid refractive index changes within the sucrose solutions. After these bulk solution refractive index changes have been subtracted from the experimental data (green circles), the OR data is expected to be flat, as was found for the alcohol-water mixtures. Any remaining changes in the OR data suggest additional behaviour not directly included in our two-part description. These changes are likely to be due to approximations made within our simple description of the

OR response; such as assuming that the bulk concentration remains constant right upto the silica surface.

If the bulk solution is inhomogeneous, especially adjacent to the silica surface, then the assumptions for our two-part description of the OR will be invalid. The OR will be very sensitive to any local inhomogeniety near to the surface since this is the basis of how the instrument is set up to measure adsorption isotherms. Over the range of sucrose concentrations examined in Figure 6, the viscosity of the bulk solution has increased by 35% [18], suggesting that some associative structures have indeed formed within the bulk solution [19, 20]. These solution molecular structures (probably associated with hydrogen bonding in the water [19]) are expected to be depleted from the silica interface by a distance comparable to their size [21]. The molecular size of a sucrose molecule is 1.06 nm [20], which is well within the sensing zone of the OR and is consistent with the dimensions of adsorbed surfactants that are routinely measured using this approach. The depletion length is expected to be sucrose concentration dependent [21], and will decrease at increasing sucrose concentrations. However, the rate of change of concentration with distance should increase as the concentration increases. The likely effect of this decrease in depletion length with the associated increase in the change of concentration over distance, will be to increase the measured value of $\Delta S/S_0$ since at small separations from the silica surface, the sucrose will behave in a similar manner (although opposite in character) to a weakly adsorbed layer. The greater the degree of inhomogeniety within the near surface sucrose solution, the larger the deviation measured by the bulk corrected $\Delta S/S_0$.

Now we examine the case of a non-adsorbing solution that may contain well-defined structures. OR data for sodium dodecylsulphate (SDS) over a similar concentration range to that explored with the CTAB are plotted in Figure 7.

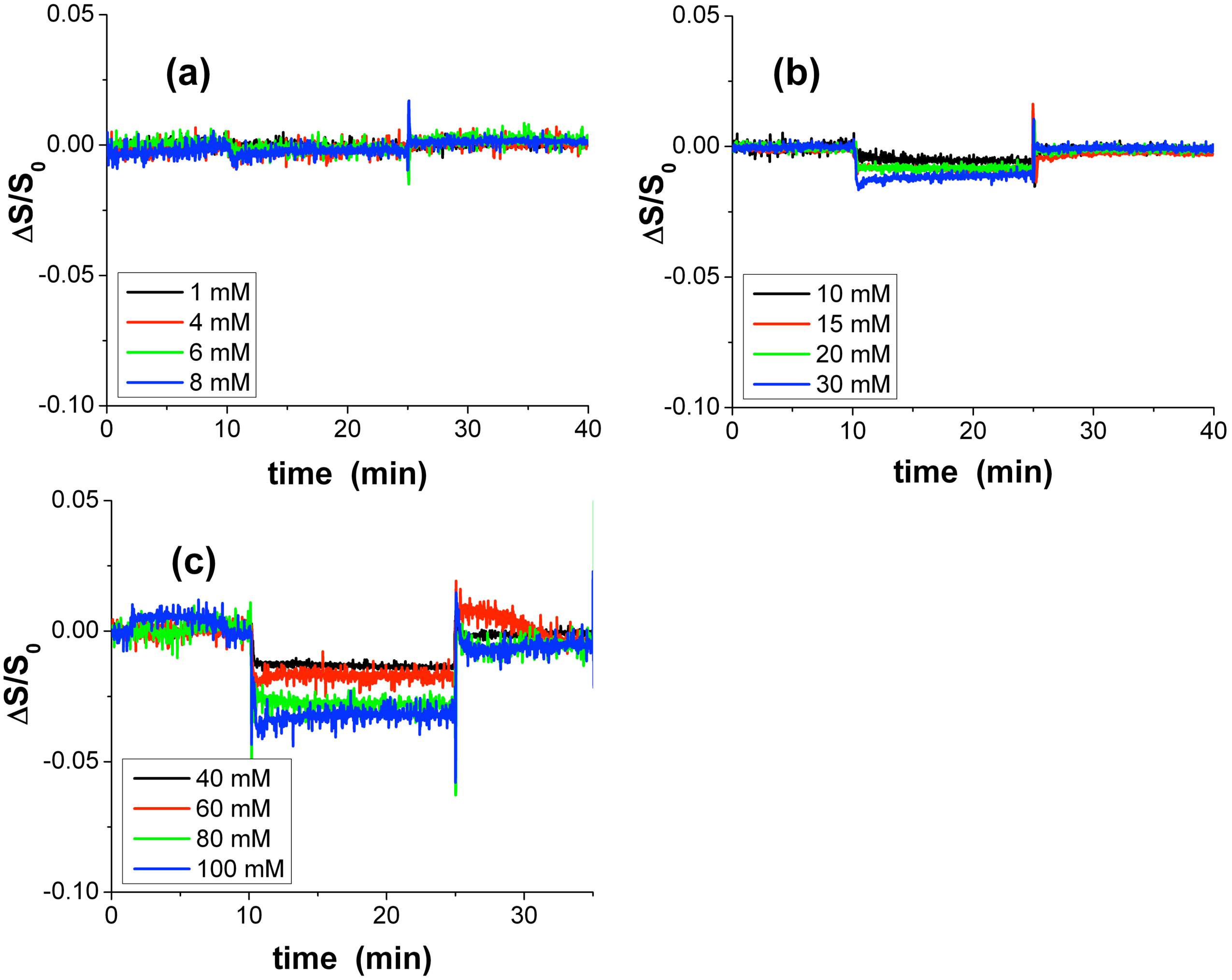

**Figure 7:** Adsorption profiles for SDS in water by OR, (a) upto the cmc, (b) at medium SDS concentrations and (c) at high SDS concentrations.

As for the sucrose, SDS does not adsorb directly onto silica surfaces and so, once the solution refractive index has been taken into account, we expect no further change in $\Delta S/S_0$ to be measured. Our two-part description, equation (1), has $(\Delta S/S_0)_i = 0$ in this case. The cmc for SDS is around 8 mM, where spherical micelles are formed in the bulk solution. A dn/dC of 0.1397 g/mL was used to calculate the bulk SDS solution refractive index values. A summary of the data plotted in Figure 7 are shown in Figure 8.

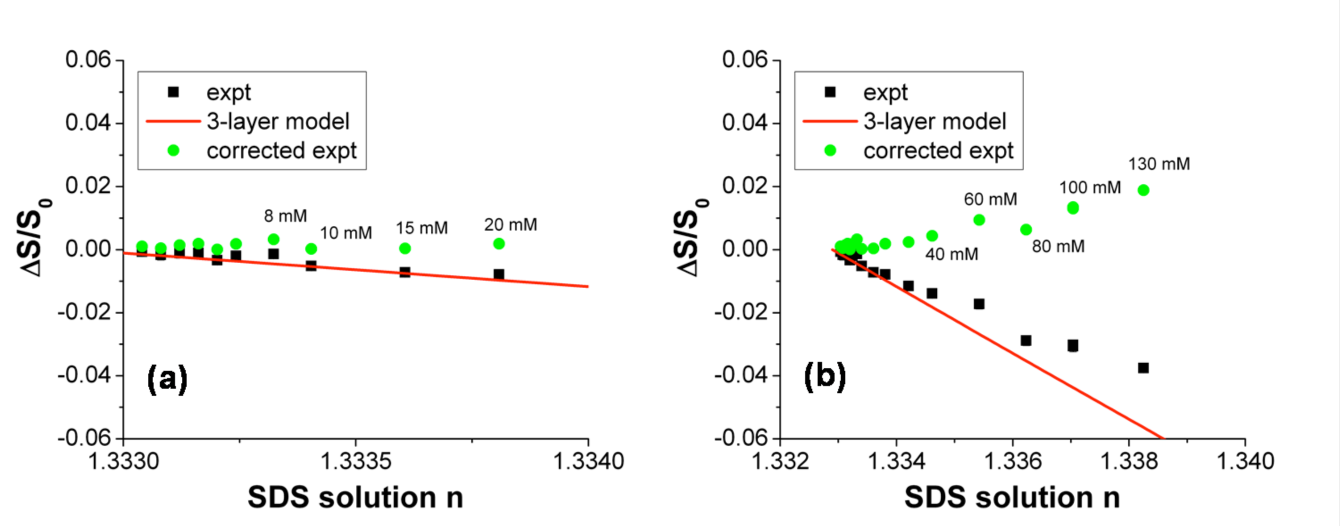

**Figure 8:** Changes in $\Delta S/S_0$ versus the SDS solution refractive index as measured by OR. (a) lower concentrations and (b) the entire concentration range examined. Raw data (black squares) are presented alongside the 3-layer model of the bulk solution (red line) and the bulk refractive index corrected data (green circles).

Figure 8(a) shows that, once corrected for the bulk refractive index changes, the OR data below and near the cmc for SDS (8 mM) are essentially invariant (green circles). As the water used in this work was at pH 7, the silica surface is negatively charged and so the SDS should be depleted from the silica-water interface. Despite the simplifications made in our two-part description of the OR, equation (1), Figure 8(a) demonstrates that upto approximately 20 mM, the response of the OR agrees with a two-part description.

At higher SDS concentrations, Figure 8(b), the bulk refractive index corrected OR data again deviate significantly from zero in a similar manner to that seen for the sucrose system. In this case, the presence of charged micelle aggregates in the SDS solution and their depletion from the interface may explain these data. Earlier work for non-adsorbing polyelectrolytes, particles and surfactants at the solid-liquid interface using colloid probe microscopy has shown how structural and depletion effects can be detected even at very low concentrations. [21] The depletion of SDS micelles from the silica-water interface is clearly influencing the measured OR data in this case. These data show that when depletion from an interface is present, the OR may be capable of detecting this depletion through changes in the measured signal that do not fit with bulk solution behaviour.

It is interesting to note that we might expect at higher concentrations to also observe depletion for the CTAB example discussed earlier. At full adsorption, we expect the silica substrate to be completely coated and the surface charge to now reflect the charge on the CTAB. We may therefore expect that a depletion layer will exist between this surface adsorbed layer and the bulk solution. Interestingly, our OR arrangement is insensitive to this layer and we are not able to detect it. Obviously, the optical contrast between the adsorbed CTAB film and the bulk CTAB solution is very small and it seems that the presence of a very thin depletion layer (as it must be at such high CTAB concentrations) between these layers is not detectable with our instruments current sensitivity.

Whilst we have shown that the OR may be capable of detecting the presence of a depletion layer at the solid-liquid interface due to the presence of non-adsorbing species in the bulk solution, we have not yet found a simple route to analyse the data to extract what is commonly referred to as the ‘depletion layer thickness’. For simple adsorption, a 4-layer slab model allows determination of the adsorbed mass by assuming a thickness for the adsorbed film and a constant refractive index in that film. To model a depletion layer is more complex for a number of reasons: the layers may be relatively thick, the concentration and refractive index varies considerably across the layer, and longer range structural effects may also be present. Development of routes to better analyse these depletion data is currently the subject of further work within our research group.

## 4. Conclusions

OR data have been presented for both adsorbing and non-adsorbing systems over a wide range of concentrations on a hydrophilic silica surface. We have proposed a simple two-part model for understanding the general response of the OR to these different solutions. Usually at low solution concentrations, the first part of our model (to represent the interfacial response) shows either the normal isothermal behaviour for an adsorbing system (CTAB), or no response for a non-adsorbing system such as SDS. We have shown that at higher solution concentrations the second part of our model (representing the bulk response of the OR) begins to dominate. For simple systems such as an alcohol-water mixture, the OR response fits the expected bulk solution behaviour corresponding to the change in the refractive index of the solution as predicted by a 3-layer slab model. However we have also demonstrated that for other non-adsorbing systems such as sucrose solutions and non-adsorbing surfactants such as SDS, the OR response is not so simple.

To investigate this complex response in more detail, we have extracted the refractive index changes in the bulk solution from the OR data obtained at high solution concentrations and found the following: (a) for the adsorbing CTAB solutions the higher concentrations showed little or no signal change upto 120 mM, (b) for both sucrose and SDS solutions a gradual change in $\Delta S/S_0$ occurs at the highest concentrations investigated. We suggest that the OR is detecting depletion effects at these high concentrations. At present we are investigating ways of extracting depletion layer thickness values from these data, which could prove to be a powerful addition to the current uses of OR.

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