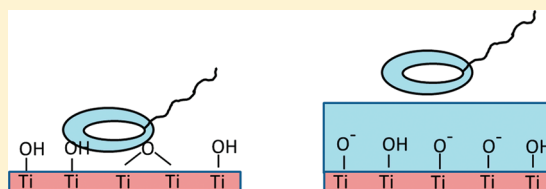


# Adsorption of Nonionic Surfactants with Ethylene Oxide Headgroup Chemistry at the Titania–Water Interface

Shannon M. Notley<sup>†,‡,\*</sup><sup>†</sup>Department of Applied Mathematics, Research School of Physics and Engineering, Australian National University, Canberra 0200 ACT, Australia<sup>‡</sup>Faculty of Life and Social Sciences, Swinburne University of Technology, Hawthorn 3122 VIC Australia

**ABSTRACT:** The adsorption of nonionic surfactants such as poly(ethylene oxide) alkyl ether surfactant ( $C_nE_m$ ) and polysorbate (commonly referred to as Tween) was studied at the titania–water interface using optical reflectometry and atomic force microscopy (AFM). Previous reports have indicated little to no adsorption of these surfactants to titania, however under certain conditions, the surface excess was high. Typically significant adsorption was only observed when the titania surface was not strongly hydrated, that is, at point of zero charge and under low ionic strength conditions. For these amorphous titania surfaces prepared using atomic layer deposition, the pzc was at pH 5.1. Furthermore, the adsorbed amount of nonionic surfactant decreased with increasing ionic strength. This was attributed to the increased hydration of the titania interface from the specific adsorption of ions inhibiting the adsorption of the strongly hydrated ethylene oxide headgroup of the surfactant. AFM force measurements at the pzc in the presence of the surfactant as a function of concentration confirmed adsorption of the surfactant. Furthermore, soft contact imaging suggests that there was a spherical aggregate adsorbed layer structure above the critical surface aggregation concentration at pH 5.1 and no additional background electrolyte. No structure was observed at lower concentrations or under other solution conditions.



## INTRODUCTION

Surfactants are used in a variety of industrial applications as a means for the facile modification of interfacial properties. In particular, the adsorption of surfactants at the solid–liquid interface may result in altered wettability, a key property used for enhanced mineral recovery through froth flotation or in detergency.<sup>1</sup> Typically surfactants are classified by the chemistry of the headgroup: that is, cationic, anionic, zwitterionic or nonionic. The properties of surfactants in solution or at the liquid–vapor interface have been intensively studied. More recently, techniques for measuring the interaction of surfactants at the solid–liquid interface have become more sophisticated and more sensitive allowing the unambiguous determination of adsorbed layer structure.<sup>2</sup>

The structure of adsorbed surfactant aggregates at the solid–liquid interface is closely related to aggregates in solution where the dimensions of the surfactant molecules, in terms of headgroup size and tail length, together with the magnitude of intermolecular forces impose the geometry.<sup>3,4</sup> Additionally, though, the nature of the interface will also be influential. The adsorbed layer structure of surfactants to many solid substrates has been investigated. These include both hydrophilic mineral surfaces such as silica,<sup>5–13</sup> mica,<sup>14,15</sup> and cellulose,<sup>16–18</sup> as well as hydrophobic surfaces such as highly oriented graphite<sup>19</sup> or self-assembled monolayers.<sup>20</sup>

Unlike surfactants with charged headgroups where the adsorption is predominantly due to Coulombic interactions, the driving force for nonionic surfactants is more subtle on hydrophilic surfaces.<sup>11,21–25</sup> Typically, hydrogen bonding

between the surfactant headgroup and solid–liquid interface has been suggested as the mechanism for the adsorption of nonionic surfactants. If this is the only important factor, then all of these classes of surfactants (such as alkoxyether, maltosides, sorbitan esters etc.) should interact equally well with all hydrophilic substrates capable of hydrogen bonding. However, throughout the literature, there are a number of notable exceptions. For instance, maltoside based surfactants adsorb weakly onto silica but strongly onto titania yet surfactants with ethylene oxide headgroups show the reverse trend.<sup>26</sup> Surfactants with ethylene oxide headgroup chemistry are extensively used throughout industry however the poor adsorption to the titania–water interface is an issue yet to be fully understood. Part of the reason for the fewer studies involving titania is due to the relatively high roughness of commercially available surfaces. However, recent developments in thin film technology, in particular atomic layer deposition, now allow the production of titania surfaces of sufficient smoothness for use in many surface sensitive techniques such as reflectometry and surface forces measurements. Furthermore, the crystallinity of such surfaces may also be well controlled through simple altering parameters such as temperature during preparation.

The adsorption of surfactants to titania is of significant interest as a means to control the wetting properties,

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particularly as titania is commonly used in ceramics or as a pigment or opacifier in many coatings. Mattsson et al suggest that water inhibits the adsorption of ethylene oxide surfactants to surfaces such as titania due to preferential hydrogen bonding.<sup>27–29</sup> Both the surface and surfactant are strongly hydrated under most normal solution conditions hence the ability to replace a strongly bound water molecule at the interface with a surfactant molecule from solution is limited. Stubenrauch et al also suggest that headgroup hydration is an important factor along with the flexibility of the hydrophilic chain.<sup>26</sup> It stands to reason then if the hydration of either the titania–water interface, or the surfactant headgroup, can be reduced, then enhanced adsorption could be observed. This study will use a combination of optical reflectometry and atomic force microscopy to demonstrate that nonionic surfactants with ethylene oxide headgroup chemistry can adsorb strongly to the titania–water interface under certain solution conditions, specifically when the titania surface is least hydrated which is at the point of zero charge.

## ■ EXPERIMENTAL SECTION

**Materials.** Two nonionic surfactants were used in this study. Hexaethylene glycol monotetradecyl ether ( $C_{14}E_6$ ) was used as received from Nikko Chemicals Co Ltd. (Japan). Polysorbate 20 (Tween 20) was used as received from Sigma-Aldrich. Milli-Q water was used to prepare the surfactant solutions with the pH adjusted using an appropriate amount of HCl or NaOH. NaCl were used to prepare the solutions of varying ionic strength and were used as received from Sigma-Aldrich Australia.

Oxidised silicon wafers were obtained from Peregrine Semiconductors (Sydney, Australia). An oxide layer thickness of 107 nm was thermally grown onto the silicon wafer surface. Titania surfaces were then produced by atomic layer deposition (ALD) on top of this silica precursor layer. A Savannah thermal ALD system from Cambridge Nanotech was used. Typically, a 5 nm thick amorphous titania layer was deposited at 110 °C using ALD by using alternating cycles of water priming layer followed by titanium. Nitrogen was used to purge the system between pulses of water (0.015 s) and the precursor (0.12 s). The thickness of the films was confirmed using ellipsometry. The same titania surfaces were used in both the adsorption measurements using the optical reflectometry technique and the direct imaging of surfactant layer structure using the atomic force microscope (afm). Furthermore, silica particles (~10  $\mu$ m diameter) were coated with  $TiO_2$  for use in the measurement of the electrophoretic mobility.

**Methods. Optical Reflectometry.** Optical reflectometry (OR) was used to determine the surface excess and adsorption kinetics of the nonionic surfactants to the titania thin film. In OR,<sup>30–32</sup> silicon wafer with a well-defined oxide layer (107 nm) and a thin titania layer deposited at the solid–liquid interface is used as the substrate. A polarized laser beam is passed through a 45° prism onto this reflective silica surface. The laser beam is reflected back through another 45° prism into the detection system where the parallel (p) and perpendicular (s) components are measured. Changes in the optical properties due to an adsorbing species will alter the ratio of the p and s components. This ratio can be converted to a surface excess by using a four layer optical model (silicon:silica:adsorbing species:solvent), if the refractive indices and layer thicknesses are accurately known.<sup>33</sup> The refractive indices used in calculating the sensitivity factor were  $n_{Si} = 3.8$ ,  $n_{SiO_2} = 1.46$ ,

$n_{TiO_2} = 2.5$ ,  $n_{surf} = 1.44$ , and  $n_{water} = 1.33$  with the refractive index increment ( $dn/dc$ ) for  $C_{14}E_6$  of 0.135 mL/g and Tween 20 of 0.140 mL/g used.<sup>17,25,34,35</sup> Using this technique, the adsorption of the surfactants to titania is performed under well-defined hydrodynamic conditions with the incident laser beam striking the surface at the stagnation point with a constant flow of polymer solution supplied to the liquid cell. Thus, the adsorption is diffusion limited. Hence, OR gives valuable information regarding the surface excess as well as adsorption kinetics and has been extensively used to study the interaction of surfactants and polymers to the solid–liquid interface.<sup>2,17,36–45</sup> All measurements were performed at 24 °C.

**AFM Imaging and Force Measurements.** Adsorbed surfactant layers were imaged using “soft contact” atomic force microscopy.<sup>7,14–16</sup> Typically, the greatest force (highest set-point) is used prior to the tip pushing through the surfactant layer onto the underlying substrate. Force calibration is used to determine the optimum set-point. Lower set-points tend to reduce the observed contrast of the features of the surfactant layer. A Multimode SPM (Veeco Inc., USA) was used for these measurements. Standard, contact  $Si_3N_4$  cantilevers (Veeco, USA) were used for all measurements in this study. The data were typically collected using the 200  $\mu$ m long, triangular shaped cantilever with a spring constant of 0.07 N/m as measured by the thermal noise method.<sup>46</sup> The scan rate was typically between 5 and 10 Hz and gains of between 1 and 2. Force–distance curve were also measured at various stages throughout the experiments to ensure that adsorption of the surfactant occurred. Concentrations of surfactant were typically above the critical surface aggregation concentration (csac) with 2 times the critical micelle concentration (cmc) chosen to ensure that an equilibrium structure is achieved quickly. The cmc for  $C_{14}E_6$  is 0.01 mM and for Tween 20 is 0.08 mM.

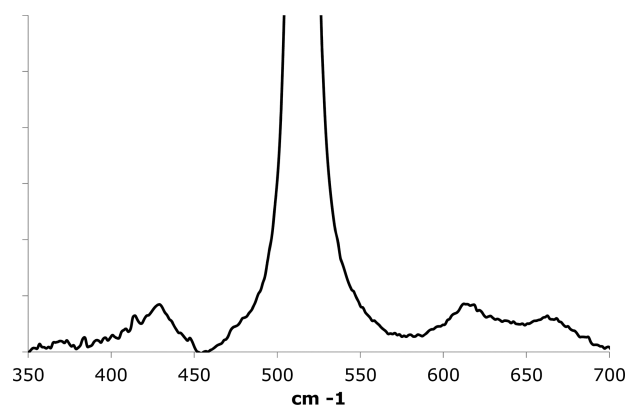
**Electrophoretic Mobility.** The electrophoretic mobility of silica particles coated with titania deposited using ALD under the same conditions as described above was determined using a Malvern Zetasizer Nano complete with autotitrator. A minimum of three different determinations of the electrophoretic mobility was performed as a function of increasing pH in order to determine the point of zero charge.

**Raman Spectroscopy.** The titania thin films supported on the oxidized silicon wafer were characterized using Raman spectroscopy with a Horiba Jobin Yvon T64000 Raman system. Laser excitation at 532 nm was used.

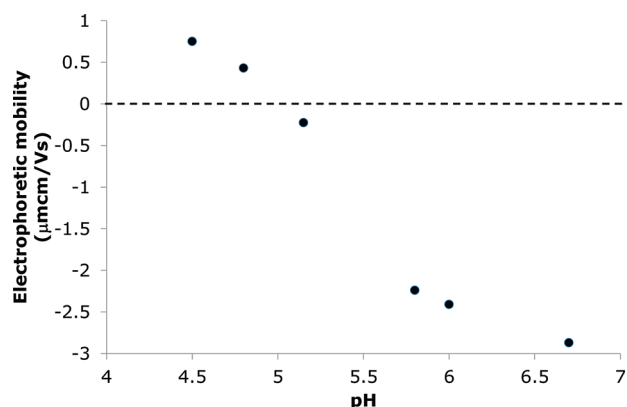
## ■ RESULTS AND DISCUSSION

Prior to the measurement of surfactant adsorption to the titania–water interface, the thin films prepared using ALD were characterized using Raman spectroscopy to determine if the procedure produced amorphous or crystalline titania phases. Figure 1 shows the spectrum recorded over the range 350–700  $cm^{-1}$ . Two broad and weak peaks centered at 430 and 610  $cm^{-1}$  were observed along with the sharp peak at 520.6  $cm^{-1}$  attributed to the underlying silicon substrate. The two broad peaks are indicative of an amorphous titania phase,<sup>47,48</sup> as expected given the low temperature at which the film was deposited.<sup>49</sup>

The charge on the titania surface was also investigated as a function of pH. The electrophoretic mobility of titania coated silica spheres is shown in Figure 2. At high pH, the titania surface has a measured mobility that is net negative and at low pH, it is positive. From this data, the point of zero charge (pzc)



**Figure 1.** Raman spectrum of the 5 nm thick film of titania supported on a silica substrate prepared using atomic layer deposition.

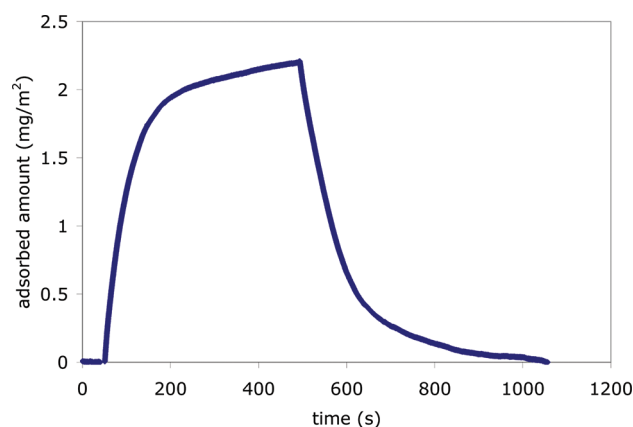


**Figure 2.** Electrophoretic mobility of the titania coated silica spheres as a function of pH in a background electrolyte of NaCl with a concentration of 1 mM.

was found to be at pH 5.1 in a background NaCl solution with a concentration of 1 mM. The pzc determined here agrees well with previous studies<sup>50–57</sup> of titania as well as surface prepared using the same technique.<sup>58</sup>

Two nonionic surfactants were used in this study to probe the influence of the overall headgroup size on the adsorption at the titania–water interface. These were a “simple” poly(ethylene oxide) alkyl ether surfactant ( $C_{14}E_6$ ) and polysorbate (commonly referred to as Tween 20). Both of these surfactants have ethylene oxide headgroup chemistry however the Tween 20 surfactant has a significantly larger hydrophilic component with 20 ethylene oxide groups distributed in four chains linked together by the sorbitan group. Typically, both surfactants have been characterized as having poor adsorption to the titania–water interface.

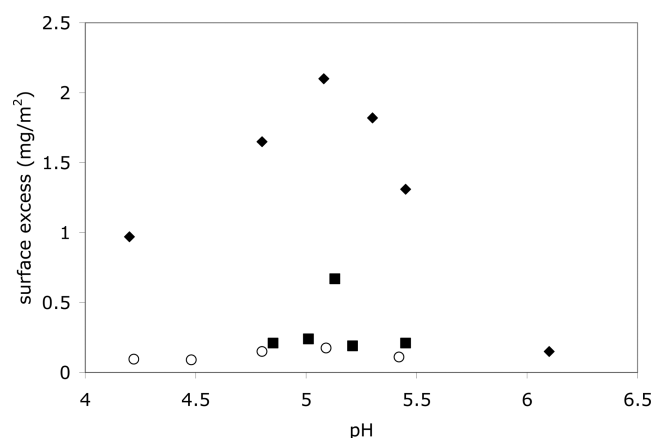
The kinetics of adsorption of  $C_{14}E_6$  to the titania surface was determined using optical reflectometry and the data from a typical experiment is shown in Figure 3. Prior to the introduction of a surfactant solution, a baseline is recorded using the same aqueous solution conditions. At ambient pH (6.0) and with no added electrolyte, little surface excess is observed. Decreasing the pH of the solution to approximately that required to give the titania no net charge resulted in a dramatic increase in adsorbed amount of the surfactant using a solution with concentration of  $2 \times \text{cmc}$ . The surfactant rapidly adsorbs to the interface up to an equilibrium plateau value. The form of the adsorption data was consistent for all of the surfactant solutions investigated here. After equilibrium was



**Figure 3.** Adsorption kinetics of  $C_{14}E_6$  to the titania–water interface at pH 5.1 measured using optical reflectometry. A baseline in pH adjusted water is first recorded followed by injection of the surfactant at 30 s. Once equilibrium is reached, the pH adjusted water is injected again at 480 s (15 min adsorption) in order to monitor the desorption kinetics and demonstrate that complete desorption of the surfactant layer occurred.

reached, the surfactant was rinsed from the surface using the same background aqueous solution used to collect the baseline. In this way, the kinetics of desorption could also be investigated. In all cases, complete desorption of surfactant from the titania–water surface was achieved.

While there is no change in the chemistry of the surfactant in this pH range, the negative charge on the titania surface decreases and eventually becomes positive at pH < 5.1. The equilibrium adsorbed amount of a  $2 \times \text{cmc}$  solution of  $C_{14}E_6$  at varying pH is shown in Figure 4. The overall hydration state of



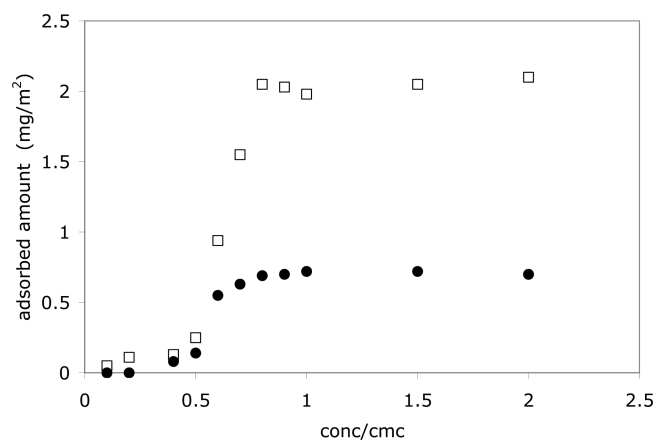
**Figure 4.** Adsorption of a  $2 \times \text{cmc}$  solution of  $C_{14}E_6$  to the titania–water interface studied as a function of pH for varying concentrations of added NaCl as a background electrolyte: 0.1 mM (diamonds), 1 mM (squares) and 10 mM (circles).

the ethylene oxide species of the surfactant headgroup should remain constant under these conditions. However, the hydration of the titania surface may reasonably be expected to be altered along with the change in surface charge. This is particularly true at the point of zero charge where the titanium–oxygen bonds adopt a crown-ether type spatial arrangement rather than titanium–hydroxyl bonding. At pH conditions on either side of the pzc, the surface groups are hydroxylated or charged, giving a greater potential for

interaction with water molecules with much stronger hydrogen bonding ability. Interestingly, the data in Figure 4 shows that the adsorption of the  $C_{14}E_6$  surfactant to the titania surface is surprisingly sensitive to the solution pH. That is, even a change of as little as 0.1 of a pH unit is sufficient to reduce the overall equilibrium surface excess dramatically. The influence of a background electrolyte (NaCl) is also shown in Figure 4. Again, the presence of even a small concentration of competing ions into the solution is sufficient to reduce the equilibrium surface excess of  $C_{14}E_6$  to the titania–water interface. Furthermore, the overall adsorbed amount decreases with increasing ionic strength. It should be noted that the pzc is not expected to change significantly with the low concentrations of added NaCl used here. The pH range studied as shown in Figure 4 is broad enough that so that any small variations in the pzc with added electrolyte would be encompassed.

The surfactant solubility is also not substantially influenced by the presence of NaCl up to concentrations of 0.01 M as is typical for many ionic surfactants. At much greater ionic strength, the ethylene oxide groups may start to dehydrate, particularly for added salt in excess of 0.25 M.<sup>59</sup> There is also some evidence based on the solubility of poly(ethylene oxide) that suggests that chaotropic cations and anions have a greater ability to induce dehydration of the ethylene oxide groups leading to a reduction in the lower critical solution temperature which lowers solvency.<sup>60</sup> This is of more concern for surfactants with larger ethylene oxide hydrophilic headgroups than for the relatively short  $E_6$  for the surfactant used here as solubility could be significantly affected. The specific ion effects on the adsorption of nonionic surfactants are currently under investigation and will not be discussed further here.

The maximum adsorbed amount of  $C_{14}E_6$  was observed at the pzc (pH 5.1) and with no added electrolyte for surfactant concentrations well above the cmc. Figure 5 shows the



**Figure 5.** Adsorption isotherm for  $C_{14}E_6$  at the titania–water interface at pH 5.1 with added background electrolyte of 0.1 mM (open symbols) and with 1 mM NaCl (closed symbols) using OR.

adsorption isotherm as a function of concentration under these solution conditions. Similarly to isotherms for the adsorption of  $C_{14}E_6$  to both silica and cellulose, the measured surface excess using optical reflectometry shows a characteristic step-like profile.<sup>17</sup> That is, very little surfactant is adsorbed below the critical surface aggregate concentration (csac) which is about  $0.8 \times \text{cmc}$ . Above the csac, adsorption to the titania–water interface occurs co-operatively with a maximum in adsorbed amount of  $1.85 \text{ mg/m}^2$  observed. This corresponds to

an area per surfactant molecule of  $51 \text{ Å}^2$  which is similar to that observed previously for adsorption to the silica–water interface.<sup>17,25</sup> Figure 5 also shows the adsorption isotherm for  $C_{14}E_6$  in a background electrolyte solution of NaCl with a concentration of 1 mM. Even above the csac, the surface excess is low, with no detectable adsorption observed using surfactant solutions of concentration less than 0.4 mM.

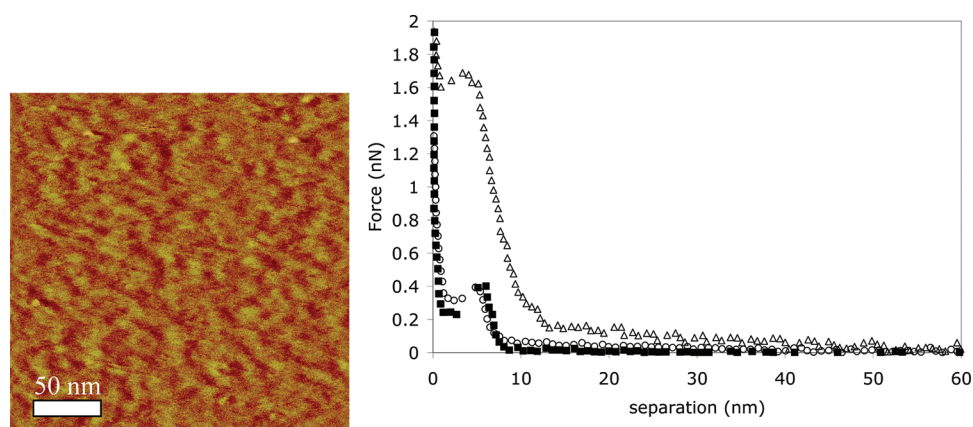
Atomic force microscopy soft contact imaging was used to investigate the structure of the adsorbed layer at the optimum solution conditions for achieving the maximum in adsorbed amount of  $C_{14}E_6$ . Figure 6 shows an image for the adsorption at  $2 \times \text{cmc}$  at the pzc (pH 5.1) with no added electrolyte. Similarly to hydrophilic surfaces such as silica and cellulose, the image shows surfactant aggregates at the titania–water interface indicating co-operative adsorption under these solution conditions. Adsorption to the titania surface can be confirmed by observing the corresponding surface forces measurements, also shown in Figure 6. The force–distance curves on approach are shown at different surfactant concentration. At a concentration above the csac, the “push-through” distance is approximately 6 nm and is consistent with previous measurements using the same surfactant.<sup>17</sup> Also apparent is the longer repulsion at greater surface separations most likely due to the double layer repulsion.

The adsorption of a nonionic surfactant with a much larger hydrophilic headgroup bearing 20 ethylene oxide units, Tween 20, to the titania–water interface was also investigated using optical reflectometry. Again, the influence of the surface characteristics due to variations in the solution pH was studied. Figure 7 shows the adsorbed amount of Tween 20 as a function of pH with no added electrolyte to the system. As can be seen here, there is a significantly lower surface excess observed than for the  $C_{14}E_6$  under equivalent solution conditions. The maximum in adsorbed amount is much less than what could be described as a monolayer. Interestingly, though, the position of the maximum adsorbed amount with pH was again at the pzc indicating that while minimal adsorption occurs under any conditions, the greatest surface excess is when the surface is charge neutral and least hydrated.

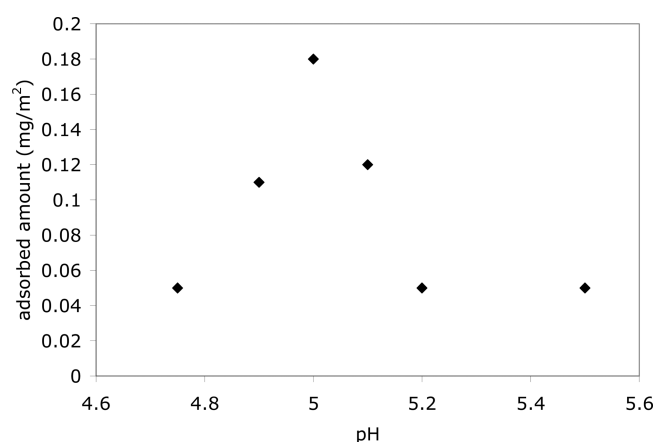
To confirm the adsorption of Tween 20 to the titania–water interface, surface forces measurements were also undertaken. Even though there is little adsorption, there is an observable change in the forces on approach under solution conditions which maximizes the adsorbed amount, that is, at the pzc and no added electrolyte. Figure 8 shows the measured force–distance curve between the  $\text{Si}_3\text{N}_4$  afm tip and the titania surface. No imaging was performed as the surface excess was well below monolayer coverage. It is possible that the forces shown in Figure 8 are due to the adsorption of surfactant to the afm tip, rather than the titania surface. However, considering the optical reflectometry data, it is most likely that there is a weak adsorption to the surface. Furthermore, the titania surface after exposure to the surfactant was no longer completely wetting indicating an increased hydrophobicity due to the orientation of surfactant tail groups away from the interface.

The data presented in Figures 3–8 clearly show that under certain solution conditions that nonionic surfactants with poly(ethylene oxide) headgroup chemistry do adsorb at the titania–water interface. The surface excess is particularly sensitive to the nature of the charge and hydration of the titania–surface. Adsorption is maximized at the pzc. Large headgroups do result in significantly decreased adsorbed amounts which are at the limit of detection. The surface excess

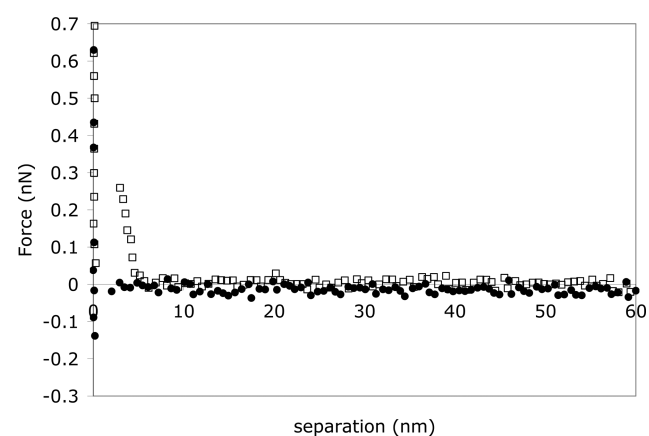




**Figure 6.** Left: AFM soft contact deflection image of the adsorbed layer of  $C_{14}E_6$  to the titania–water interface at pH 5.1 with no added electrolyte ( $z$  scale is 1 nm). Right: Force–distance curves on approach for a  $Si_3N_4$  tip to the flat titania substrate at pH 5.1 as a function of  $C_{14}E_6$  surfactant concentration.



**Figure 7.** Adsorption isotherm for Tween 20 at the titania–water interface as a function of solution pH with no added electrolyte.



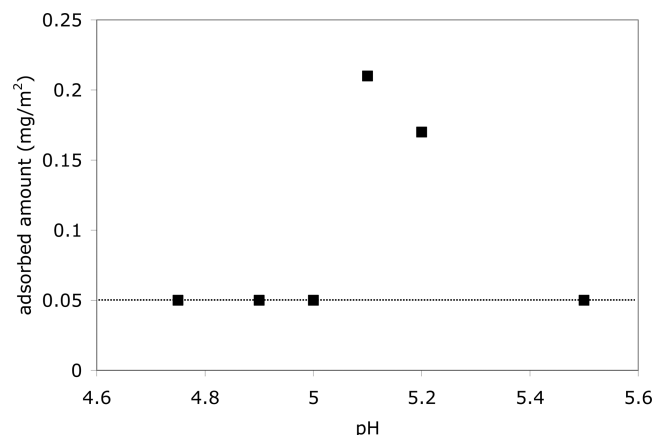
**Figure 8.** Force–distance curves on approach for a  $Si_3N_4$  tip to the flat titania substrate at pH 5.1 in water (closed circles) and in  $2 \times$  cmc solution of Tween (open squares) also at pH 5.1.

measured using the optical reflectometry technique is about an order of magnitude greater in sensitivity than previously reported measurements using similar surfactants with ellipsometry which indicated little to no adsorption, specifically under ambient solution conditions.

The change in adsorbed amount with pH is somewhat surprising given previous data for the adsorption of nonionic

surfactants to other hydrophilic surfaces such as silica and cellulose. It should be apparent though that titania has a comparatively larger potential dispersion interaction than either silica and cellulose, hence the attractive nature of a strongly bound layer of water molecules. At pH either side of the pzc, the hydrogen bonding interactions with water are further promoted with enhanced donor and acceptor sites above and below, respectively. This, however, is no different to that case of the silica–water interface, hence the dispersion interaction can be considered to be the dominating factor for the difficulty in replacing the hydration of the interface with surfactant molecules. Thus, the strength of the interaction between titania and water is minimized at the point of zero charge, indeed it is reduced to such an extent that adsorption of the strongly hydrated headgroup of the nonionic surfactant molecules can displace the water molecules. This is only when the headgroups are sufficiently small.

To test this hypothesis, the adsorption of poly(ethylene oxide) with a molecular weight of 75 kDa to titania was also investigated as a function of pH. Figure 9 shows that little to no adsorption occurred except again at the pzc, indeed the surface excess that was determined was at the noise limit of the optical reflectometry instrument for all other pH tested. Therefore, the



**Figure 9.** Adsorption of PEO (MW 75 kDa) to the titania–water interface studied using optical reflectometry as a function of pH. A background electrolyte with concentration of 0.1 mM was used. The dashed horizontal line is the noise limit for the instrument.

size of the hydrophilic headgroup is an important factor governing whether the poly(ethylene oxide) surfactants will adsorb to the interface.

The decrease in adsorbed amount of the nonionic surfactant with the addition of salt is surprising. The background electrolyte, NaCl, is not expected to have a significant influence on the hydration of the surfactant, particularly at the concentrations used here (0.01 M and below). Furthermore, if it were to cause removal of water molecules from the ethylene oxide headgroup, an increase in the adsorption may be expected to result due to the decreased solubility of the surfactant molecules in water. The observed decrease in the adsorption of these nonionic surfactants to the titania–water interface is probably due to the strong dispersion interactions between the surface and the hydrated ions. An increase in the background electrolyte concentration gives rise to competitive adsorption and a comparatively more favorable interaction of the ions with the surface than the ethylene oxide surfactant headgroups to the surface. Hence hydrated ions are more efficient at displacing bound solvent molecules than the surfactant molecules.

## CONCLUSIONS

Nonionic surfactants with ethylene oxide headgroup chemistry have been observed to adsorb at the titania–water interface however only under solution conditions where the hydration of the surface is minimized. That is, adsorption is a maximum at the point of zero charge. Surface charge only plays an indirect role in determining the extent of the adsorption of these nonionic surfactants promoting the binding of water at the surface inhibiting the uptake of surfactant molecules at the interface. These observations indicate that the adsorption of nonionic surfactants to a hydrophilic surface is strongly influenced by both pH and ionic strength even though electrostatic mechanisms are not the dominant factor determining the overall surface excess.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: snotley@swinburne.edu.au. Telephone: +61 392148635.

### Notes

The authors declare no competing financial interest.

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