Chapter 4

The effect of temperature on adsorbed morphologies of nonionic surfactants

4.1 Introduction.

Controversy persists regarding the explanation for the phenomenon of non-ionic surfactant clouding at a defined temperature, $T_c$. The unusual feature of this phase separation in non-ionic micellar solutions is that it occurs as temperature is increased, in contrast to the more conventional phase separation as temperature is reduced. In this more usual case, the energy of interaction between the constituents dominates over entropy, and a condensed phase is stabilised as temperature is lowered.

Although the clouding phenomenon of nonionic solutions has been discussed by many authors\textsuperscript{150-157}, questions about its origin and the influence of temperature on micellar size remain. Early light-scattering experiments on dilute aqueous solutions of polyoxy(ethylene) oxide surfactants show a considerable increase in scattered light intensity with temperature\textsuperscript{158,159}. The traditional explanation for these results is that the micellar aggregation number increases with temperature, with a negligible role played by non-ideality effects. The argument for micellar growth with temperature is based on the assumption that two ethylene oxide segments within the micelle repel each other at low temperatures when both these segments are hydrated, and become attractive with increasing temperature because of dehydration. This reduces the effective area per polar group and causes a growth in size of the spherical micelle to
longer and longer rods. Interpretation of these results assumed the solutions to be ideal and ignored the effect of intermicellar interactions on apparent size distributions.

However, as it is known that the approach to the critical point in binary mixtures is accompanied by long-range concentration fluctuations, and hence by a large light-scattering cross section, the observed phenomena are, at least partially, explainable by the existence of consolute phase boundaries\textsuperscript{160,161}. This argument has been used to discuss minimal micellar growth with increase in temperature and has been supported by neutron scattering experiments\textsuperscript{162,163}, and transient fluorescence experiments\textsuperscript{164} on C\textsubscript{12}E\textsubscript{6}.

These opposing viewpoints on micellar growth and its importance on the clouding phenomenon have since been reconciled. A theoretical framework encompassing the effect of both intermicellar interactions and multiple chemical equilibria on the micellar size distribution and on the equilibrium thermodynamic properties in the two-phase regions of micellar solutions\textsuperscript{155-157,165} has been devised.

The classical mechanism explaining clouding is that nonionic surfactant micelles interact via an attractive (van der Waals) potential whose well depth increases with temperature\textsuperscript{166}. At T\textsubscript{c}, these micelles attract each other and form clusters\textsuperscript{152}. When two micelles collide at T\textsubscript{c}, they can adhere to each other for a limited period of time before thermal energy disrupts the bonds again. The possibility of adhesion over short time intervals would lead to non-random spatial distributions as observed in clusters. A plausible mechanism giving rise to such forces would be micellar hydration properties. At low temperatures, the ethylene oxide units are well hydrated and this bound water would prevent interpenetration of headgroups of neighbouring micelles. At higher temperatures, dehydration would induce
intermicellar hydrogen bonding through shared water molecules associated with the headgroups\textsuperscript{151}.

More recently, an alternate explanation for criticality in non-ionic surfactant microemulsions involving the formation of densely branched networks\textsuperscript{167} has been extended to include binary non-ionic surfactant and water systems. With increasing temperature a sphere to rod transition is driven by a reduction in the water accessible headgroup area which is favoured by the hydrophobic effect reducing the interfacial area per molecule\textsuperscript{168}. At higher temperatures, junctions appear which are lower in free energy when compared with end-cap free energy. The number of these thermally generated junctions increases, resulting in the formation of larger and larger branched aggregates of rods\textsuperscript{169}. Upon reaching a critical number of junctions, a connected network spanning the entire volume of the system is formed.

The induced attraction for 3-fold junctions is strong enough to drive a first-order phase transition of purely entropic origin. The junction-dominated, high density phase is of higher entropy despite the translational entropy of the chains being lower in the high density phases\textsuperscript{170}. This leads to a phase separation between a densely connected network and a dilute phase of almost unbranched micelles\textsuperscript{169,170}, triggered by the increase in configurational entropy of the large number of junctions.

The observation of phase coexistence between dilute and dense network phases by cryo-TEM\textsuperscript{1} provided visual evidence for the existence of these branched networks in the vicinity of the cloud temperature. This study also confirmed that at the boundaries of the bicontinuous regime, the networks break up into disconnected cylindrical globules. This shows that junctions are preferred at low values of spontaneous curvature while ends are preferred at larger spontaneous curvatures.
Cryo-TEM is a very useful technique for visualising morphologies within the bulk. On a surface, atomic force microscopy (AFM)\textsuperscript{2,171} has similarly proven a very powerful tool for visualising surfactant morphologies. From a number of different studies examining surfactant structures under different conditions\textsuperscript{2,50,58,172}, factors that control aggregate structure in the bulk have been found to be applicable to interfacial structures. Silica is a surface well studied\textsuperscript{67} with respect to surfactant morphology and is a substrate observed to have a low influence on adsorbed structures. For instance, DTAB\textsuperscript{36} and CTAB\textsuperscript{60} form globules on silica as in solution, whereas hemimicelles are formed on graphite and cylinders or bilayers on mica. Similarly, non-ionic surfactants that aggregate into spherical micelles in solution are also observed to form globules on silica\textsuperscript{173}, again compared to hemicylinders on graphite. However, even a relatively benign surface such as silica can influence interfacial morphologies merely by enhancing surfactant concentrations and forcing their arrangement on a planar substrate. This needs to be considered when interpreting any AFM results and translating them to behaviour in the bulk.

This chapter uses AFM to examine the morphological transition of several non-ionic surfactants adsorbed onto silica at different temperatures. Polyoxyethylene surfactants adsorb to the silica interface through hydrogen bonding with surface silanol groups\textsuperscript{38}. The mesh-like morphology discovered at intermediate curvatures to cylinders and bilayers and described in Chapter 3 has motivated this AFM examination into non-ionic surfactant morphologies as a function of temperature. Using AFM, the adsorbed surfactant structure as the cloud temperature is approached has been studied; primarily on hydrophilic silica with some studies performed on hydrophobic graphite for comparison.
4.2 Materials and Methods

Pentaethylene glycol monododecyl ether (C\textsubscript{12}E\textsubscript{5}), hexaethylene glycol monotetradecyl ether (C\textsubscript{14}E\textsubscript{6}), hexaethylene glycol monohexadecyl ether (C\textsubscript{16}E\textsubscript{6}), triethylene glycol monododecylether (C\textsubscript{12}E\textsubscript{3}), octaethylene glycol monododecyl ether (C\textsubscript{12}E\textsubscript{8}) and octaethylene glycol monotetradecyl ether (C\textsubscript{14}E\textsubscript{8}) were purchased from Fluka and used as received. Polyoxyethylene 23 lauryl ether, (Teric G12A23, analogous to Brij35) was provided by Orica Australia, and contains a distribution of ethylene oxide chains about a mean of 23. This was used as received. All solutions were made in Milli-Q water.

AFM experiments were performed on both hydrophilic silica (Silicon Valley Microelectronics Inc., CA) and graphite (Advanced Ceramics Corporation). Immediately prior to each experiment involving graphite, a fresh surface was produced by stripping the top layers of graphite with adhesive tape. The silica surface was cleaned by rinsing with copious quantities of deionised water and ethanol, irradiated under UV for 30 minutes and soaked in a 1w% NaOH solution for 1 minute to re-establish hydrophilicity of the surface. The silica was cleaned in exactly the same manner for all experiments performed on this surface.

The surfactant film was imaged using the soft-contact method described in Chapter 1.1. Temperatures were controlled in a similar manner as described in Chapter 2.
4.3 The effect of temperature on morphologies adsorbed on silica.

Using AFM, the morphologies of three surfactants, $C_{12}E_5$, $C_{14}E_6$ and $C_{16}E_6$ each with a cloud point at a temperature accessible within the experimental setup (40ºC) were studied. Other non-ionic surfactants with cloud temperatures above 40ºC were also studied up to this maximum temperature. The results of all these experiments are summarised in Table 4.1.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Cloud point</th>
<th>Structure at 20ºC.</th>
<th>Structure at 35 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{12}E_5$</td>
<td>31 ºC</td>
<td>Spheres</td>
<td>Mesh</td>
</tr>
<tr>
<td>$C_{16}E_6$</td>
<td>38 ºC</td>
<td>Spheres</td>
<td>Mesh</td>
</tr>
<tr>
<td>$C_{14}E_6$</td>
<td>40 ºC</td>
<td>Spheres</td>
<td>Mesh</td>
</tr>
<tr>
<td>$C_{14}E_8$</td>
<td>71 ºC</td>
<td>Spheres</td>
<td>Rods</td>
</tr>
<tr>
<td>$C_{12}E_3$</td>
<td>-</td>
<td>Bilayer</td>
<td>Bilayer</td>
</tr>
</tbody>
</table>

Table 4.1: Summary of structures formed by $C_nE_m$ surfactants on silica at 20ºC and at 35ºC.

Figure 4.1 displays AFM deflection images of $C_{16}E_6$ on silica at three different temperatures. At 21ºC this surfactant forms globules (4.1a) of periodicity 10.4 nm, which agrees with results previously published. Increasing the cell temperature to 25ºC resulted in a film transformation to short rods (4.1b). Raising the temperature to 30ºC resulted in a morphology change to a mesh structure (4.1c). For this surfactant the mesh was observed from temperatures below the cloud point (38ºC) and, further increase in temperature did not alter the morphology from a mesh.
Figure 4.1: AFM deflection images of 0.12 mM (50 cmc) C_{16}E_{6} on silica showing an adsorbed morphology of globules at 20ºC (a), rods at 25ºC (b) and a mesh at 30ºC (c).

A similar curvature progression was observed for C_{14}E_{6} on silica (Figure 4.2). At 22ºC, globules were again observed with a slightly smaller periodicity of 9.2 nm. The effect of temperature was again a reduction in curvature to rods at 26ºC and then a mesh for temperatures 30ºC and above.

Figure 4.2: AFM deflection images of 0.05 mM (5 cmc) C_{14}E_{6} on silica showing an adsorbed morphology of globules at 22ºC (a), rods at 26ºC and a mesh at 30ºC.

The last surfactant studied in this manner, C_{12}E_{5}, also showed the same progression. At 21ºC, globules with a periodicity of 7.3 nm were formed. Increasing temperatures similarly resulted in a transformation to rods at 28ºC and a mesh at
30°C. The solution remained clear at this temperature, however, very rapidly turned cloudy with a slight increase in temperature.

![Figure 4.3](image)

**Figure 4.3:** AFM deflection images of 0.12 mM (2 cmc) C\textsubscript{12}E\textsubscript{5} on silica showing an adsorbed morphology of globules at (a) 21°C, rods at 28°C (b) and a mesh at 30°C (c).

The morphology of all of these surfactants reduced in curvature with temperature and was a gradual process. Elongation of spheres into rods proceeded via formation of short rods and the evolution of the mesh was preceded by a region of branched rods. However, not one surfactant was observed to transform to a planar bilayer structure even above the cloud point. A similar temperature experiment was performed on C\textsubscript{12}E\textsubscript{3}, which forms a lamellar phase in solution and a bilayer on the surface. The bilayer structure formed by this surfactant was unaltered by variation in temperature on the surface (Figure 4.4).
Figure 4.4: AFM deflection images (300x300 nm) of 0.13 mM C$_{12}$E$_3$ at (a) 22ºC and (b) 30ºC.

Structures formed by surfactants with cloud points above the experimentally accessible maximum of 40ºC were also studied. Figure 4.5 shows AFM deflection images of C$_{14}$E$_8$ at 22ºC, 28ºC and 32ºC. At 22ºC, the morphology of C$_{14}$E$_8$ is globular, as expected from previous results$^{173}$. Increasing temperature to 32ºC resulted in a reduction in curvature from globules to rods, which is consistent with the progressions observed in Figures 4.1 to 4.3. All results are summarized in Table 4.1.

Figure 4.5. AFM deflection images of C$_{14}$E$_8$ adsorbed to silica at (a) 22ºC, showing a globular morphology, at (b) 28ºC elongated globules or short rods and (c) at 32ºC, rods.
Force curves for these surfactants revealed only minor changes to the interaction between the tip and surface with temperature variation (Figure 4.6). For C\(_{12}\)E\(_5\) and C\(_{14}\)E\(_6\), single jumps into contact from approximately 4 nm and 4.3 nm respectively, were observed (Figures 4.6a and b). However, two repulsive walls were observed for C\(_{16}\)E\(_6\) at separations 7.1 nm and 1.1 nm (Figure 4.6c). In a previous AFM study\(^{173}\) on nonionic surfactants on silica, a similar double repulsive force profile was observed, however the surfactants on which a double repulsive wall was observed were different. For instance, in this paper,\(^{173}\) C\(_{12}\)E\(_5\) and C\(_{14}\)E\(_6\) displayed a double repulsive barrier whereas C\(_{16}\)E\(_6\) did not. The opposite is observed in this study and, contrary to this previous study, at all imaging pressures only the one structure was observed.

A similar double repulsive barrier has also been observed on adsorbed C\(_{12}\)E\(_5\) films on silica in a colloid probe AFM study\(^{174}\). In this study, the morphology of the film was not directly determined and a bilayer morphology assumed. The outer force wall was considered due to steric interaction between the two intercalated bilayers. The inner force wall was therefore where the outer layers were removed and the two surfaces in monolayer – monolayer contact. However hemifusion is unlikely to occur in these systems, where the adsorbed layer morphology is not a bilayer.\(^{175,176}\)
Figure 4.6. Representative force curves at different temperatures for (a) 0.12 mM C$_{12}$E$_5$, (b) 0.05 mM C$_{14}$E$_6$ and (c) 0.12 mM C$_{16}$E$_6$.

Polyoxyethylene surfactants are soluble in water due to hydrogen bonding of the solvent with the ether oxygens of the headgroup. Raising temperature dehydrates the surfactant headgroups and, as they lose solubility, headgroup size is reduced. This increases the surfactant packing parameter$^{52}$ and reduces aggregate curvature. This is clearly shown in the results presented on silica. However the film never transformed
to a bilayer prior to the cloud temperature. This means that when the cloud temperature was reached, the morphology of the film was a mesh and not the structure of lowest possible curvature, a bilayer. With respect to current discussions on the mechanism of clouding in the bulk, the results described above are significant. Particularly the concept that at $T_c$ a densely branched network of cylindrical micelles exist in solution$^{1,177}$. In the results presented in Figures 4.1 to 4.5, there was clearly an elongation in the adsorbed micelle structure with increase in temperature. Not only did the spherical micelles elongate into cylindrical micelles as $T_c$ was approached, a densely branched mesh structure was observed for three different surfactants at temperatures immediately prior to the cloud point.

The same surfactants were studied on graphite as temperatures were again increased towards the cloud temperature. Graphite is known to strongly dictate adsorbed morphologies through epitaxial binding of the surfactant alkyl chain templating a hemicylindrical structure.

### 4.4 The effect of temperature on adsorbed morphologies on graphite.

The effect of temperature on structures formed by these surfactants was also studied on the graphite cleavage plane. On graphite, the influence of the surface is much more pronounced with most conventional surfactants adsorbing as hemicylinders$^{2,37-39}$. The basal plane of graphite consists of sheets of hexagonal rings of carbon atoms with a threefold axis of rotation. The interaction between the substrate and alkyl chain via hydrophobic and van der Waals interactions orient the alkyl chain on a zigzag line connecting nearest-neighbour carbon atoms on graphite. This interaction with linear alkyl chains is the sole defining feature in aggregate morphology for a large range of surfactants with different molecular geometries. For
most surfactants, straight hemicylinders are observed\textsuperscript{173}, an example of which is displayed for C\textsubscript{16}E\textsubscript{6} in Figure 4.7. No change in structure was observed for C\textsubscript{16}E\textsubscript{6}, C\textsubscript{14}E\textsubscript{6} and C\textsubscript{12}E\textsubscript{5}, with increase in temperature to T\textsubscript{c}. Despite there being a loss of headgroup hydration and reduction in headgroup size with increase in temperature, this was insufficient to force surfactant morphologies into any other structure than hemicylinders. The strong van der Waals interaction between the surface and alkyl chain of the surfactant continued to dominate aggregate morphology.

![Figure 4.7](image)

**Figure 4.7** AFM deflection image of the adsorbed morphology of 2 cmc C\textsubscript{16}E\textsubscript{6} on graphite at (a) 23°C and (b) 30°C. No change in this hemicylindrical morphology was observed with variation in temperature.

One of the instances where surfactants adsorb to graphite in morphologies differing to hemicylinders is when headgroups are large and bulky such as C\textsubscript{12}E\textsubscript{23}. This surfactant form a featureless monolayer (Figure 4.8a) because the large headgroup inhibits the formation of hemicylinders\textsuperscript{39,47} by causing mis-match in the graphite - alkyl chain registry. Increasing the temperature to 28°C, however, transformed the film to hemicylinders. That is, curvature apparently increased with temperature. This is contrary to the results presented on silica where temperature affected a reduction in film curvature and highlights the influence of the surface.
When temperatures were cooled back down to 22ºC, the film did not return to a featureless monolayer, as expected, and the hemicylindrical morphology persisted.

![AFM deflection images showing the change in morphology with temperature of 0.2 mM (2 cmc) C_{12}E_{23} on graphite. At 22ºC a monolayer was observed (a) and at 28ºC hemicylinders (b). These hemicylinders persisted even after temperatures were cooled back to below the initial starting temperature of 22ºC.](image)

**Figure 4.8.** AFM deflection images showing the change in morphology with temperature of 0.2 mM (2 cmc) C_{12}E_{23} on graphite. At 22ºC a monolayer was observed (a) and at 28ºC hemicylinders (b). These hemicylinders persisted even after temperatures were cooled back to below the initial starting temperature of 22ºC.

Either the increase in temperature sufficiently reduced headgroup size to allow registry between the surface and the alkyl chain or hemicylinders are the equilibrium structure for this surfactant but due to the bulky, polymeric nature of the headgroup the time to equilibration is very long. To differentiate between these two possible explanations, cell temperature of a C_{12}E_{23} solution was held at 22ºC for approximately 40 hours to determine whether there was a slow rearrangement from a monolayer to hemicylinders which was not observed.

### 4.5 Conclusions

In this chapter, AFM images of adsorbed non-ionic surfactant films at different temperatures on hydrophilic silica and hydrophobic graphite have been shown. Three non-ionic surfactants with cloud points within the experimentally accessible range <40ºC were studied and all found to follow the progression of...
spheres to cylinders to a mesh at temperatures immediately before $T_c$ on silica. None of the surfactant films were observed to fully reduce in curvature to a bilayer and is discussed with respect to current theories explaining clouding in the bulk. No temperature effect was observed for these surfactants on graphite except for $C_{12}E_{23}$ where an increase in film curvature was observed. This is due to the temperature induced headgroup size reduction allowing registry with the graphite surface.