A Structural Study on the Solubilisation of Pesticides into Surfactant Micelles

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy in the Faculty of Engineering and Physical Sciences

Faheem Noorahmed Padia

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School of Physics and Astronomy
It is reported that the Prophet Muhammad (pbuh) said, "If anyone travels on a road in search of knowledge, God will cause him to travel on one of the roads of Paradise. The angels will lower their wings in their great pleasure with one who seeks knowledge. The inhabitants of the heavens and the Earth and (even) the fish in the deep waters will ask forgiveness for the learned man. The superiority of the learned over the devout is like that of the moon, on the night when it is full, over the rest of the stars. The learned are the heirs of the Prophets, and the Prophets leave (no monetary inheritance), they leave only knowledge, and he who takes it takes an abundant portion."  

Sunan of Abu-Dawood, Hadith 1631

In research there are those times when it seems as though everything has gone wrong and all your work has been a waste of time. But in those moments one just needs to reflect on the above lesson for it teaches us that no matter where your studies have taken you it is the very act of seeking knowledge that is worthy of rewards... Then when your mind is at ease it all becomes clear, the reason nothing makes sense is because you're using the wrong blooming equation!
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Abstract

A Structural Study on the Solubilisation of Pesticides into Surfactant Micelles

Faheem Noorahmed Padia  University of Manchester  Doctor of Philosophy, 2012

The ability of surfactants to form micelles and solubilise hydrophobic substances in aqueous environments has been widely exploited in formulation science. In spite of extensive studies over the past few decades by both experimental and theoretical methods, however, it remains difficult to predict key micellar parameters such as their size, shape and nanostructure which is essential for their successful implementation in the solubilisation of active ingredients. This is partly due to the vast number of surfactants commercially available but, in addition, the fragmentation of the field of surfactant science, over recent years, has made it more difficult to identify general trends and properties of surfactant systems. A further challenge is in characterising systems of heavily mixed surfactants since our knowledge on pure surfactant systems may not allow us to predict the behaviour of these systems. The broad aim of this thesis was to contribute to these aspects of surfactant science.

The first part of the thesis reports a systematic study of the surfactant structure-micellar structure relationship of pure alkyl ethoxylate (CₘEₙ) surfactants. This was done by independently varying the lengths of the alkyl chain and ethoxylate group and measuring the micellar structural properties. The next part of the thesis reports the effects of solubilisation of two model pesticides, Cyprodinil and Diuron, on the size, shape and internal structure of these surfactant micelles. These pesticides were chosen because they were structurally representative of different features of those widely used in agrochemicals. The final part of the thesis reports the work on binary surfactant mixtures that rationalise the general structural features of mixed micelles and their impact on pesticide solubilisation. Various experimental techniques were used including small angle neutron scattering (SANS), nuclear magnetic resonance (NMR), nuclear Overhauser effect spectroscopy (NOESY NMR), dynamic light scattering (DLS) and UV spectroscopy.

The key findings of the thesis were that the micellar core volumes could be predicted with reasonable accuracy using the hydrophilic-lipophilic balance (HLB) of the surfactants in pure micelles. NOESY results revealed protrusions of the terminal methylene groups into the ethoxylate shell, thus providing evidence for the theoretically predicted phenomenon referred to as the ‘surface roughness’ of the core-shell interface. SANS revealed that solubilisation of both pesticides caused micellar growth, with the long axial lengths of the micelles growing much longer. These structural changes were associated with the dehydration of the ethoxylate shells. Although a partitioning experiment predicted that the pesticides would be solubilised in the hydrated ethoxylate micellar shell, NOESY measurements revealed that the solubilisation occurred predominantly in the micellar cores. The discrepancy was caused by alkyl chain-ethoxylate mixing leading to the formation of dehydrated palisade regions that entrapped the pesticides towards the cores. The results from the binary mixed micelles showed some signs of synergistic behaviour but no enhancement of pesticide solubilisation.
Declaration

No portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning

Faheem Noorahmed Padia
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1 Introduction

1.1 Surfactants in Agrochemicals

People outside the fields of chemistry and soft matter physics will not be too familiar with the family of molecules known as surfactants but these amphiphilic molecules play a huge role in our daily lives. They are not only used in the manufacture of many commercial products such as detergents, cosmetics, paints and pharmaceuticals but they are also heavily used in industrial processes such as in the clean-up of oil spills and the remediation of contaminated soils. As a result, approximately 10 million tons of surfactants are used each year. While this figure is quite staggering in itself, to really demonstrate the importance of surfactants we draw attention to the impact of surfactants in the field of agrochemicals.

Historically, agricultural pest control was achieved using basic inorganic substances derived from natural sources such as arsenical compounds, cobalt, mercury and sulphuric acid\(^1\). But as the usage of these substances grew, their harmful effects on humans began to manifest, driving the development of newer and safer substances. With the emergence of the chemical industry a 2\(^{nd}\) generation of pesticides was introduced in the 1940's with dichloro-diphenyl-trichloroethane (DDT) being the standout discovery. The low cost and improved efficacy of these new synthetic pesticides led to their quick adoption. However, their heavy use over time led to widespread pesticide resistance. As a result, a 3\(^{rd}\) generation of pesticide active ingredients (AIs) was developed in the 1970's and 80's. These were even safer and more effective than the 2\(^{nd}\) generation AIs but the increasing complexity of their molecular structures meant that they generally exhibited poorer aqueous solubility, making it more difficult to prepare them as formulations. This
prompted the introduction of surfactants as formulation aids into agrochemicals.

Initially, surfactants were used just to aid the dissolution of low solubility substances in solution. But extensive studies in surfactant science led to a better understanding of their solution behaviour which, in turn, led to their increased use in pesticide formulations. Nowadays, surfactants are used extensively to enhance various formulation properties such as wetting and spreading, formulation stability and in some cases also to enhance the efficacy of AIs. Accordingly, surfactants have become an integral component of all pesticide formulations.

One may be wondering at this point why this particular example has been chosen to illustrate the importance of surfactants since pesticides are more commonly associated with environmental damage. To answer this, we refer to three simple findings from studies on the influences of pesticides:

1. it has been estimated that there could be a 75% increase in the cost of fruit & vegetable production if pesticides were not used\(^2\),
2. up to 50% of the produce could be lost in transportation and storage without pesticides\(^3\) and
3. 65% - 200% extra land would be required to meet current demands for produce from organic production (i.e. without the use of pesticides) due mainly to lower yields.\(^4\)

Thus, reducing the use of pesticides would not only significantly impact the cost and quality of food but it would also effectively make it impossible to produce the required amounts. One only needs to reflect on the catastrophic effects the shortage of food had during the global food crisis of 2008\(^5\) to appreciate how big an impact pesticides (and, by extension, surfactants due to their integral role in modern pesticide formulations) have on our lives.
1.2 Surfactant Micelles

Surfactants have many useful solution properties which all stem from their amphiphilic structures. The opposing forces experienced by the different parts of the molecules in aqueous solution causes them to behave rather unusually. Although their general behaviour has been characterised well over the years there is one particular property that is still not very well understood and is yet to be exploited in large scale applications. That is their tendency to form micelles.

Micelles are nano-aggregates which spontaneously form in order to minimise interactions between the hydrophobic parts of the surfactants and water. As this driving force is common to all surfactants, all micelles share the same general features; they have a central ‘core’ region which is extremely hydrophobic because it contains the hydrophobic portions of the surfactants and an outer ‘shell’ which is hydrophilic since it contains the hydrophilic portions of the surfactants which extend out from the core into the bulk solvent (usually water), as illustrated in Figure 1.1. While this structure is formed as a means of minimising surfactant-water interactions (and thus system energy) it also gives rise to an incredibly useful property, the ability of micelles to solubilise hydrophobic substances while remaining thermodynamically stable in aqueous solution. This property has been known since the 1950’s but it is only in the last two decades that experimental techniques have become powerful enough to study micellar solubilisation in detail. As a result, our understanding of the solubilisation process is still far from complete.

In summary, micelles are of interest for two main reasons in agrochemical industry: as formulation aids to improve the solubility of hydrophobic AIs such as pesticides that are difficult to dissolve in water and also because micelles must already exist in pesticide formulations due to the extensive use of surfactants to enhance the efficiency and efficacy of
formulations when applied to plant leaves through improved wetting and surface interaction. This work investigated the interactions between micelles and pesticides and, in particular, focussed on the impact on pesticide solubilisation on micellar properties. The results could potentially aid both the development of future products and the improvement of the performance of the existing products.

1.3 Micelles versus Emulsions

Currently, pesticide AIs with poor aqueous solubility are most commonly prepared as emulsifiable concentrates (ECs). In terms of volume consumed ECs account for about 40% of the global usage of pesticide formulations.\(^6\) These types of formulations are popular because they are:
• Simple to formulate - ECs are prepared by dissolving AIs in a solvent (usually non-polar petroleum based, e.g. xylene) and then adding an emulsifier blend (blend of surfactants which provides good emulsification).

• Easy to prepare by consumer - the end-user only needs to dilute the EC in a spray tank before application, making them particularly easy to use.

• Able to enhance the biological activity of certain AIs - the exact mechanisms for enhancing biological activity are not yet known but ECs are known to improve the efficacy of certain AIs.\textsuperscript{6}

Despite all of the above, however, efforts are now being made to reduce the reliance on ECs mainly due to their use of harmful and dangerous petroleum based solvents. But, in addition, there are a number of other reasons why ECs are not ideal, such as:

• Solvent damage - the solvents used in ECs can damage application equipment. Rubber and plastics are particularly susceptible to damage. This is obviously inconvenient for the consumer.

• Thermodynamic instability - even with a good selection of surfactants, emulsions are inherently unstable and they will undergo phase separation over time either via flocculation, coalescence or creaming. To exacerbate this, formulations are often subjected to a wide range of temperatures (typically from -10°C to 50°C), meaning that the emulsifier blend has to provide a long life time in a fairly wide range of temperatures. If phase separation does occur it can lead to re-crystallisation of AIs which can undermine product efficacy.

• Large and polydisperse droplets - emulsion droplets in actual formulated products are generally polydisperse and relatively large (typically around 250nm or more in diameter\textsuperscript{7}). This feature not only
causes the inherent stability arising from coalescence but also makes it difficult to achieve a uniform distribution of AIs when applying the product which could potentially lead to dosage problems.

With regards to each of the above points, micellar solutions can offer far more favourable properties. Most importantly, they are thermodynamically stable so that the formulations would be less likely to degrade over time and would also provide a more uniform droplet size, providing better application efficacy and more uniform AI dosage. In addition, they can be entirely water based and thus avoid the need for non-polar solvents which can, in turn, reduce adverse impact on tools and environment.

In spite of these benefits, there is one major drawback to the use of micelles, that is, they tend to have lower solubilisation capacities than ECs. Many workers have studied ways in which the maximum additive concentration (MAC) in micellar formulations can be maximised but the AI capacities of ECs are still far superior to those achievable in micellar formulations. Overall, our current knowledge on the solubilisation capacity of different surfactants of real pesticides is very limited. This topic needs to be further addressed if micelles are to be genuinely considered for commercial application.

1.4 System under Study

The widespread use of surfactants in industry has led to the development of numerous different types of surfactants that are now commercially available. For the purpose of this study, the non-ionic alkyl ethoxylate surfactants were chosen. These are composed of a hydrophobic alkyl chain of length, m, and a hydrophilic ethoxylate group consisting of, n, ethoxylate units (-CH₂CH₂O-)_n, with general formula, CₘEₙ. These surfactants were chosen because non-ionic alkyl ethoxylates are amongst the most commonly used ones in the
agrochemical industry. In addition, the lengths of both hydrophobic and hydrophilic groups can be varied independently allowing for a systematic study of the influences of the head and tail groups. Two model pesticides, Cyprodinil and Diuron, were used as the probe solubilisates. These were chosen due to their varying molecular structure and solubility properties.

The C_mE_n surfactants have in fact been extensively studied in the past but, surprisingly, there have been few systematic studies on the properties of C_mE_n micelles. Thus, before embarking on the study of solubilisation in these micelles it was deemed necessary to first gain an understanding of the properties of the pure micelles. In particular, an attempt was made to characterise the surfactant structure-micelle structure relationship. Following this, the influences of the pesticides on the micelles were investigated to reveal the interactions between the two substances. Finally, solubilisation in binary surfactant micelles was explored. The motivation behind this was that industrial grade surfactants generally consist of a broad range of surfactant structures around some average structure. It would, therefore, be very useful to understand how solubilisation in mixed micelles compares to that in pure micelles.

1.5 Outline of Thesis

Following the introduction to the thesis as given above (Chapter 1), Chapter 2 introduces the theoretical background to micellisation and solubilisation. This provides a foundation for understanding the experimental results presented later in the thesis. In Chapter 3 the experimental techniques used in the study are discussed, including small angle neutron scattering (SANS), ^1^H-NMR and NOESY NMR, dynamic light scattering (DLS) and UV spectroscopy. In Chapters 4, 5 and 6 we present the results of all the experimental studies and discuss them accordingly. Chapter 4 reports the study of micellar properties with respect to surfactant molecular structure. In Chapter 5 the influences of
the pesticides on the micelles are discussed while in Chapter 6 the solubilisation in pure micelles is compared to that in binary mixed micelles. In Chapter 7 we propose future work both in continuation of this work but also in the field in general.
2 Theoretical Background

2.1 Surfactants

The scientist’s habit of categorising substances is well known. In formulation science, a particularly important and useful categorisation is to follow a substance’s affinity to water. Substances that are only sparingly soluble (or insoluble) in water are termed hydrophobic while substances that readily dissolve in water are called hydrophilic. Those substances that possess both hydrophobic and hydrophilic qualities are known as amphiphilic molecules. While the solution behaviour of hydrophobes and hydrophilies is well defined and easy to predict, the same cannot be said of amphiphiles. Due to the opposing forces experienced by these molecules in aqueous solution their behaviour is much more unusual. However, their unusual behaviour has proven to be extremely useful in formulation science resulting in the extensive study and rigorous characterisation of their solution behaviour. Nowadays, amphiphiles are an essential component in the formulation sphere.

Many of the key properties of amphiphiles arise from their tendency to assemble or aggregate at surfaces and interfaces as illustrated in Figure 2.1. As a result of this high surface activity amphiphiles were termed ‘surface active agents’ which was later shortened to surfactants. The surface activity of surfactants is spontaneous and occurs as a means of expelling the hydrophobic moieties in the molecules from the aqueous environment (and thus reduces the total solution energy). However, the consequences of the behaviour can be quite significant. For example, the aggregation of amphiphiles at the air-water interface reduces the surface tension of water leading to the easier formation of bubbles and spreading of droplets. The aggregation of amphiphiles at the surface of hydrophobic molecules in aqueous solution, on the other hand, can
Figure 2.1 – Surfactants accumulate at interfaces in order to expel the hydrophobic portion from the aqueous environment. This has the effect of reducing surface tension. If a hydrophobic substance is also present in the solution surfactants can attach to the surface hydrophobic molecules forming emulsion droplets.

act to stabilise the hydrophobes and help to disperse them which is the basis of emulsification. It is these properties that have proven to be so useful in industry.

Today surfactants are used in industry to fulfil various functions. In some commercial products they are used simply to manipulate solution properties but in other products surfactants comprise the core ingredients. Their widespread use has resulted in the development and commercial availability of vast ranges of surfactants with greatly varying molecular structures. This being said, the hydrophobic portion of most surfactants tends to be a hydrocarbon chain and it is the structure of the attached hydrophilic group that is varied. Accordingly, surfactants are categorised by the properties of the hydrophilic group and in particular the head group charge. There are four main surfactant types:
• **Anionic surfactants** - the hydrophilic group carries a negative charge. These are the most used surfactants in industry. Common examples include alkylbenzene sulphonates which are used in detergents and sodium dodecyl sulphate (SDS) (Figure 2.2a) which is used in toothpastes, shampoos and cleaning products.

• **Cationic surfactants** - positively charged amphiphilic group. These surfactants are used much less frequently than anionic surfactants but dodecyl trimethyl ammonium bromide (DTAB) is an example of a commonly used cationic surfactant (Figure 2.2b).

• **Nonionic surfactants** - uncharged amphiphilic group. After anionic surfactants these are the second most widely used surfactants in industry. The most common type of non-ionic surfactants is the alkyl ethoxylate family in which the amphiphilic group consists of a number of repeating ethoxylate subunits (-CH₂CH₂O-) (Figure 2.2c). These are widely used in biological applications due to their relatively high biocompatibility. The hydrophobic portions of ethoxylated surfactants are often varied too with common classes being alkyl ethoxylates, alkyl phenol ethoxylates and fatty acid ethoxylates.

• **Zwitterionic surfactants** - hydrophilic group carries both positive and negative charges. Phospholipid surfactants (with the di-chain analogues being the building blocks of cell membranes) are zwitterionic (Figure 2.2d) but these surfactants are less used in industry so far, though they offer some fantastic properties such as far better biocompatibility to proteins and cells than non-ionic surfactants.

The general structures of surfactants with a long hydrocarbon chain and a small hydrophilic group (except in alkyl ethoxylates) has led to the hydrophobic and hydrophilic parts being referred to as the tail and head, respectively. We will follow this convention in the remainder of this work.
While it is convenient to categorise surfactants by their head group charge, in practice this system of categorisation is not particularly useful since the solution properties of surfactants are related to their overall structures as opposed to only the head group. This was recognised by Griffin and in the early 1950’s he developed a much more relevant classification system called the hydrophile-lipophile balance (HLB). In essence, the HLB attempts to quantify the overall hydrophobic nature of a surfactant by accounting for the opposing influences of water on the hydrophilic head and the hydrophobic tail.

In the case of surfactants with a hydrocarbon tail hydrophobicity is analogous to lipophilicity i.e. oil-loving.
tail. For non-ionic alkyl ethoxylate surfactants this was achieved using the following simple expression,

\[ \text{HLB} = \frac{\% \text{mass}_{\text{EO}}}{5} \]  

(2.1)

where \( \% \text{mass}_{\text{EO}} \) is the weight percentage of the ethoxylate (EO) head group. According to this definition, HLB values range from 0 – 20 with low HLB values corresponding to hydrophobic surfactants and high HLB values referring to hydrophobic surfactants.

HLB was originally used to aid the selection of surfactant mixtures that would present good emulsifying properties. It was empirically determined that water-in-oil emulsifiers exhibit low HLB values in the range of 3 – 8 and oil-in-water emulsifiers have HLB values about 8 – 18. Later, HLB was more widely adopted in industry as a general indicator of a surfactant’s properties due to its excellent correlation with surfactant solution behaviour. In Griffins own words:

“HLB is useful because it allows a prediction of the action of a surfactant”.

The limitation of Griffin’s definition of HLB to alkyl ethoxylate surfactants drove other workers to develop alternative, more general expressions. An example of such an attempt was that published by Davies. His expression could be used to calculate the HLB of any surfactant as it quantifies the HLB values of both the head and tail groups. The expression is given by

\[ \text{HLB} = \sum g_{\text{hydrophilic}} + n \times g_{\text{hydrophobic}} + 7 \]  

(2.2)

where \( g \) is the empirically determined group number of the head and tail group and \( n \) is the number of \(-\text{CH}_2-\) groups in the hydrophobic tail. \( g \) values for different types of molecules can be found in literature. It was shown that Eqn.
(2.2) produces HLB values that are consistent with experimentally determined values.

Despite the extensive use and importance of HLB in formulation science micellar properties have seldom been discussed with regards to surfactant HLB. This is rather surprising since much of the work on micelles has been focussed on their industrial applications. There is, however, one notable exception, it was a study by Diallo et al. in which the core volumes of a series of C_{12}E_n micelles were plotted as a function of HLB.\textsuperscript{11} It was found that the micellar core volumes were very sensitive to HLB when HLB < 11, then for 11 < HLB < 13 the core volumes reached a plateau and for HLB > 13 there was little change in micellar core volume. As the study was limited to a series of fixed tail length surfactants, however, it is not clear whether the trend that was observed is a general one relating to all C_mE_n micelles or only the C_{12}E_n series. One of our aims was to explore this relationship between HLB and micellar properties in more detail.

### 2.2 Micellisation

When a surfactant is added to aqueous solution at extremely low concentrations it behaves much like a normal electrolyte in that it disperses uniformly in the solution. At some slightly higher concentration the energetically unfavourable interactions between the hydrophobic tails and water start to drive the surfactant molecules to the surface in order to expel the tails from the aqueous environment giving rise to their high surface activity. Since the movement of the surfactants to the surface is thermodynamically driven free monomers in the bulk remain in equilibrium with the monomers at the surface. Increasing the concentration further eventually leads to saturation of the surface. At this point, a third regime is entered and surfactant monomers begin to spontaneously self-assemble into organised aggregates called micelles.
The concentration at which this occurs is, therefore, aptly named the critical micellar concentration (cmc).

As with the movement of surfactants towards the air-water interface, micellisation also occurs in order to reduce the interactions of surfactant hydrophobic tails with water. Thus micelles remain in equilibrium with free and interfacial monomers. Figure 2.3 illustrates the typical scenario in an aqueous solution of surfactant above the cmc. Since the bulk and interfacial regions are saturated further addition of surfactants above the cmc leads to an increase in micellar concentration while the free and interfacial monomer concentrations remain constant. At much higher surfactant concentrations more complex phases exist, but these depend largely on surfactant structure as

\[ \text{Air} \]
\[ \text{Water} \]

**Figure 2.3** – Above the cmc surfactants in aqueous solution are in equilibrium at the surface in the bulk and in micelles

\[ ^{ii} \text{The concentration of free monomers above the cmc is equal to the cmc} \]
was clearly illustrated by the phase plots derived by Mitchell et al. for various C_mE_n surfactants.¹²

Figure 2.3 illustrates the general structure of a micelle. All the hydrophobic tails collect in the centre of the aggregate to form an extremely hydrophobic core while the head groups extend out into the bulk forming a protective shell. This is the standard core-shell model of the micelles. Some of the earliest researchers who studied micelles believed that the association of hydrocarbon tails in the central core of a micelles occurred due to “like-to-like” attraction, however, Tanford later derived a phenomenological theory that showed that micellisation is in fact entropically driven¹³. According to the theory the presence of hydrocarbon tails in water causes major disruption to the ordinarily well organised packing of water molecules. But rather than breaking the relatively strong hydrogen-bonds water molecules merely adopt a new conformation at the cost of a significant loss in entropy. In order to minimise the number of water molecules involved in the re-structured conformation small clusters of disrupted water molecules begin to form¹⁴. While the clustering is enthalpically favoured it is entropically unfavourable. In fact, the entropic losses outweigh the enthalpic gains such that the clusters begin to drive hydrocarbon tails together into micellar aggregates. This eventually leads to the restoration of the normal tetrahedral structure of water. Of course, some distortion of water structure remains due to the presence of the hydrophilic head groups but the enthalpic gains from forming new bonds with these groups more than compensates for this distortion. Due to the implicit involvement of water in the process Tanford labelled it the hydrophobic effect.

One of the key points highlighted by Tanford’s theory is that aggregation of surfactants is due primarily to the hydrophobic moiety. But it also illustrates another important point. That is that it shows that cmc is a
surfactant property. Consider, for example, a surfactant with a long alkyl tail, this will lead to more significant disruption of water packing than a surfactant with a short tail. Therefore, aggregation of this surfactant will initiate at a lower concentration. Similarly, a surfactant with an extremely hydrophilic head will have a higher cmc than one with a moderately hydrophilic head because the increased favourable head group-water interactions will compensate more greatly for the unfavourable tail-water interactions.

While cmc and micellisation are strongly dependent on the hydrophobic tail, the final form of micelles (i.e. their size, shape and structure) is determined by both the head and tail groups. More specifically, it is determined by the balance between two opposing forces, one that tends to minimise the surface area of the micellar core in order to reduce the number of hydrocarbon-water interactions and another that tends to maximise the area of the shell to increase hydration of the head groups. As a result, the physical properties of surfactants are strongly dependent on surfactant molecular structure. Although previous studies on different types of surfactants have been able to show that micelles can form in a variety of different shapes and sizes including small spheres\(^{15}\), disks\(^{16}\), oblate\(^{17}\) and prolate\(^{18}\) ellipsoids and long cylinders\(^{19}\) systematic studies on the relationship between surfactant molecular structure and micellar structure have been few. As such, we aimed to get a better understanding of the relationship in this study. In the remainder of this section we discuss the well established general properties of micelles in more detail.

### 2.2.1 Micellar Structure

A lot has been learnt about the properties of the micellar core and shell over the years and some key details are discussed below. It must be noted that only single chain surfactants, i.e. surfactants with a single hydrocarbon tail and head are considered. Despite the recent interest in Gemini surfactants\(^{20}\) their
implementation in industry is still likely to be a long way off and so a
discussion of their properties is beyond the scope of this work.

**Micellar Core**

The properties of the micellar core have attracted a great deal of attention over
the years. One of the main topics of interest has been the nature of the core. On
the basis of the standard core-shell model of the micelle in which the core is
composed purely of hydrocarbon chains early researchers tended to presume
that the core has the structure and properties of a liquid hydrocarbon droplet.\(^{21}\)
Indeed, this notion was supported by a considerable amount of experimental
data. Fluorescence depolarisation measurements in which the diminution of
fluorescence polarisation of a probe molecule is measured over time were
some of the earliest indicators of the liquid-like nature. But since then other
spectroscopic methods have also been used including electron spin resonance,
Raman spectroscopy and NMR techniques. Results produced by these
methods have all tended to be consistent with the theory that the micellar core
is liquid-like.

Some studies, however, have yielded results that do not conform to this
picture. For example, Mukerjee showed that the cmc's of a homologous series
of sodium alkyl sulphates varied irregularly with chain length indicating some
partial structuring of the core.\(^{22}\) Similarly, Wolszczak and Miller found the
microviscosity's of the cores of six different Triton micelles to be in the region
of 200cP which is considerably higher than the bulk viscosity of dodecane
(1.3cP), suggesting some rigidity of the core.\(^{23}\) While this latter result could
perhaps be explained by the fact that hydrocarbon chains are anchored at the
core-shell interface giving them less fluidity than in the bulk liquid it is
interesting to see evidence for structured cores. Overall there is much more
evidence to suggest that the micellar core environment is liquid-like but it is
almost certain that the core environment is somewhat different to that of a bulk hydrocarbon due to its size and the anchoring of tails at the core-shell interface.

Another topic that has been the centre of much discussion is to what extent water penetrates the core. Given that the core is like a liquid hydrocarbon and hydrocarbons are immiscible in water it is presumable that no water penetrates into it. This was the view of Stigter who argued that water at the core interface meets a non-aqueous boundary. Molecular dynamics simulations performed by Bruce et al. also confirmed this theory. On the other hand, there is also a fair amount of experimental evidence to suggest that water does penetrate into the core. Menger et al. found using $^{13}$C NMR that water penetrates up to at least the seventh methylene in the core of KHTAB micelles. Vass et al. attempted to quantify the actual number of water molecules in the core by determining the difference in molar volumes of surfactant head and tail groups in the micellar and monomer form, it was found that there were approximately 0.45 water molecules per alkyl chain in micelles of SDS.

Clearly, there is some conflicting data on this subject making it difficult to draw any definitive conclusions. A reasonable take on the data is to say that the penetration of water into the core depends on the type of micelles and that while the core is generally non-polar it is likely that some water penetrates into the core at least up to the first couple of carbons in the tail. This interfacial penetration is most likely to be associated with the roughening of the head/ tail interface.

**Ionic Shell**

Although the main focus of this work is on non-ionic $C_mE_n$ micelles some of the key features of the ionic micellar shells are included for completeness.
In ionic micelles the presence of charges on the head groups results in the formation of an electrical double layer. The inner part of the double layer is called the Stern layer which contains all $n_{agg}$ ionic head groups where $n_{agg}$ is the aggregation number of the micelle (i.e. number of monomers making up the micelle) and $(1 - a) n_{agg}$ counterions where $a$ is the degree of ionisation of the head groups (typically about 0.2 to 0.5). The outer part of the electrical double layer is more diffuse than the Stern layer and contains the remaining $a n_{agg}$ counterions; this layer is termed the Gouy-Chapman layer (see Figure 2.4). The kinetic micelle only constitutes the Stern layer and the core and has a total charge $\pm e$ where $e$ is the elementary charge.

**Ethoxylate (EO) Shell**

In contrast to the ionic shell, the shell of non-ionic $C_mE_n$ micelles is much simpler and contains only ethoxylate chains and water molecules. The EO chains may be hydrogen bonded to water molecules but this has no noticeable effect on the actual structure of the shell.
The interfacial region between EO shell and hydrocarbon core is often referred to as the palisade layer and is believed to have interesting properties due to the contrasting properties of the core and shell. Neutron reflection studies on monolayers of C$_{12}$E$_{12}$ surfactants at the air-water interface have shown that there is considerable intermixing of head and tail groups in the palisade layer but evidence of intermixing in micelles is lacking.

The EO chains are anchored at the core-shell interface and extend out into the water. As a result, the mobility of the chain is expected to increase further away from the core. This is similar to what is observed for the alkyl chains in the core as they also experience greater mobility further away from the core-shell interface. In terms of their specific conformations, the EO chains are usually discussed qualitatively using 'zig-zag' and 'meander' models. It is thought that longer chains are more likely to form expanded helical coils (meander model) whereas shorter chains adopt fully extended (zig-zag) conformations. Additionally, hydrophilic solvents are thought to promote the meander conformation.

It was shown by Sarmoria and Blanckschtein that EO chains can be described quantitatively using standard polymer scaling laws. Interestingly, it was shown that the length of an EO chain consisting of as few as four EO units could be predicted within 4% error by the rotational isomeric state model which is used to evaluate the conformation-related characteristics of chain polymer molecules. Thus, it is reasonable to think of EO chains as polymers regardless of their length (the length in this context refers to the number of ethoxylate units in the chain).

In both the meander and zig-zag conformations the chains are generally well exposed to water; this is essential for formation of stable micelles. A number of workers have tried to quantify the exact amount of water molecules hydrating the chains. Lu et al. deduced that each EO unit is associated with
approximately 2 water molecules. Slightly higher and lower hydration values have also been proposed by other workers but 2 H$_2$O molecules per EO is about the average. This being said, it is generally accepted that increasing the ethoxylate chain length leads to an increase in hydration.

One of the problems with studies on chain hydration is that they often only reveal the average hydration of the chains. There is one notable exception, however, that is the study of Podo et al. in which the hydration of the ethoxylate units was measured with respect to their position in the shell (i.e. distance from the core) using high resolution proton NMR. It was seen that the proton peak for the surfactant head group was appreciably broadened. Upon closer inspection it was found that the peak actually constituted a number of individual peaks. For short head groups the total number of discrete peaks corresponded to the number of ethoxylate units in the head. By attributing the slight shifts in chemical shift of each of the peaks to variations in their chemical environment it was concluded that each of the ethoxylate units experienced a slightly different level of hydration. In other words, it was revealed that a hydration gradient existed in the shells of the micelles with the outermost EO being most hydrated and the ethoxylate nearer the core being most dehydrated. Although this finding seems logical this was the first time it had been observed experimentally. Figure 2.4 illustrates the difference in micellar shell structure for ionic and non-ionic micelles.

2.2.2 Micellar Shape and Size

The core-shell structure adopted by micelles significantly reduces the occurrence of energetically unfavourable hydrocarbon-water interactions. However, the tendency of the head groups to be hydrated means some interactions do still occur at the core-shell interface. These interactions could be further reduced if micelles were to grow very large but experimental
observations show that micelles are generally small aggregates indicating that some other repulsive forces must restrict the growth of micelles. Since surfactant tails are responsible for the aggregation of surfactants it is extremely unlikely that these are also the cause of repulsion, in fact it is the head groups that are the main source of surfactant repulsion.

The nature of the repulsive head-head interactions depends on the particular type of surfactant a micelle is formed by. For ionic surfactants, electrostatic interactions are the most significant source of repulsion whereas for non-ionic \( \text{C}_m\text{E}_n \) surfactants steric repulsion and the requirement for the ether oxygens to be hydrated are more significant factors. In either case, it is clear that the head and tail groups have opposite influences on a micelle with respect to micellar size. Tanford appropriately termed this behaviour, the 'Principle of Opposing Forces'\(^{13} \), and argued that the length of the hydrophobic tail and structure of the head effectively impose a lower and upper limit on the aggregation number of a micelle, respectively.

Experimental studies illustrated the respective influences of the head and tail groups on micellar aggregation number more clearly. For \( \text{C}_m\text{E}_n \) surfactants, it was found that aggregation number increases logarithmically with tail length.\(^{32} \) Increasing the head length, on the other hand, was shown to cause a linear reduction in aggregation number.\(^{33} \) Becher showed that the aggregation number of lauryl alcohol surfactants (i.e. \( \text{C}_{12}\text{E}_n \) surfactants) varied according to the following expression\(^{34} \),

\[
\text{n}_{\text{agg}} = \frac{1025}{R} - 5.1
\]  

(2.3)

where \( \text{n}_{\text{agg}} \) is the aggregation number of the micelle and \( R \) is the ethylene oxide molar ratio i.e. the number of moles of ethylene oxide per mole of hydrophobe. While the exact relationship between \( \text{n}_{\text{agg}} \) and \( R \) would presumably be slightly different for other chain lengths the key point illustrated by Becher's
expression is that chain length has a much more significant influence on $n_{agg}$ than head length.

It is interesting to note that in many of the previous studies on micellar size the sizes are most often discussed in terms of aggregation number instead of actual physical dimensions. This is partly due to the fact that aggregation number is of great importance fundamentally but in addition to this some of the experimental techniques used in early studies were simply not able to accurately determine the physical dimensions of the micelles. Nowadays, this is no longer the case and modern experimental techniques and equipment have made it possible to determine the exact physical dimensions of micelles. In spite of this, however, systematic studies on the relationship between surfactant structure and micellar size have been rare.

Similarly, there have been few systematic studies on micellar shape. One well known example was the study of Mitchell et al. in which micellar shapes for a series of $C_mE_n$ surfactants were predicted from high concentration macroscopic phase measurements. Although the predictions were based on a sound geometric-packing theory, two assumptions about the systems were also made. Firstly, it was assumed that there is hard-core repulsion between micelles which, by their own admission, was difficult to quantify and secondly, they assumed that the transition from the isotropic micellar phase to the high concentration phase was an order/disorder transition. This latter assumption was later shown to be incorrect, at least for some $C_mE_n$ surfactant systems. Thus, the reliability of the micellar shapes predicted from their work is uncertain.

While systematic studies have been few, micellar shape in general has been extensively studied. One finds, however, that the topic is filled with much controversy which stems from the fact that there are two separate theories on micellar shape that are widely accepted but propose different possible micellar
shapes. As a result, the shapes proposed in many experimental studies have depended on which theory has been used to interpret the data. This is discussed in more detail below but first it is necessary to understand why different shaped micelles exist in the first place.

One might have expected that micelles would be spherically shaped since this is the shape with the lowest energy. However, early experimental studies on micellar aggregation numbers suggested that this was not the case since the aggregation numbers tended to be larger than those allowed by spherical geometry. For a spherical shape the aggregation number of the micelle is restricted because a hole cannot exist in the centre of the micelle as this would incur an infinitely large energy penalty. Therefore, the maximum radius of a spherical micelle is limited to the length of a fully extended hydrocarbon tail, \( l_{\text{max}} \) (Å), which can be calculated using Tanford’s empirically determined expression,

\[
l_{\text{max}} = 1.5 + 1.265n_c \tag{2.4}
\]

where \( n_c \) is the number of carbons in the hydrocarbon chain of the surfactant. If one is then to assume that the micellar core has the same density of a bulk hydrocarbon (which is a reasonable assumption on the basis that the core is liquid-like as discussed above) it is possible to calculate the maximum aggregation number, \( n_{\text{max}} \), using

\[
n_{\text{max}} = \frac{4\pi l_{\text{max}}^3}{3V} \tag{2.5}
\]

where \( V \) is the volume of a single hydrocarbon chain (in Å³) which can be calculated using another expression derived by Tanford,

\[
V = 27.4 + 26.9(n_c - 1) \tag{2.6}
\]
In Eqn. 2.6 the volume of the chain is proportional to \((n_c - 1)\) instead of \(n_c\) because it is assumed that one methylene group protrudes into the shell. This is discussed in more detail later.

Using Eqns. (2.4) - (2.6) the maximum aggregation number of a spherical micelle with a C\textsubscript{12} is calculated to be about 60. But experimental studies show that the typical aggregation numbers of micelles is 50 – 100, meaning that if spherical micelles do exist they are rare.

So the next question is if micelles are not spherical then what shapes do they adopt instead? This is where the two opposing theories are introduced. On the one hand, there is Tanford’s phenomenological theory in which it was proposed that the easiest way for a micelle to accommodate more monomers was by distorting into an ellipsoid of revolution. In this case, only one dimension, the semi-minor axis, \(a_0\), needs to be constrained by \(l_{\text{max}}\) while the semi-major axis, \(b_0\), can grow to any length in order to achieve any required volume. An advantage of this model is that only small axial ratios, \(a_0 / b_0\), are required to allow for a sufficient increase in \(n_{\text{max}}\) to fit experimental data. In particular, oblate ellipsoids could allow for significant increases in \(n_{\text{max}}\) with only small distortions. Thus, according to this theory oblate ellipsoids are the most thermodynamically favourable. Robson and Dennis published findings that are consistent with this theory. They concluded from intrinsic viscosity measurements and volume calculations that the most probable shape for non-ionic Triton X-100 micelles to form was oblate ellipsoid.\(^{39}\)

Although Tanford’s theory indicated that oblate micelles are more favourable than prolate ellipsoids there is also considerable evidence to support the existence of prolate micelles. For example, Penfold et al. demonstrated excellent agreement between small angle neutron scattering (SANS) experimental data for various C\textsubscript{m}E\textsubscript{n} micelles and a prolate ellipsoid model.\(^{40,41}\)
On the other hand, there is the theory proposed by Israelachvili et al. who despite the overwhelming evidence to support the existence of ellipsoidal micelles rejected the possibility of such shapes on the basis that ellipsoids would require excessive curvature at the peripheral regions and excessive thickness in the central regions of the micelle which would be energetically unfavourable. Instead the authors justified high aggregation numbers in micelles by proposing that micelles form globular structures or oblate spheroids (i.e. the shape of red blood cells). Further, they argued that even larger micelles would form toroidal shapes and eventually infinitely long cylinders. While there is generally less experimental evidence supporting globular shapes than the ellipsoidal shapes proposed by Tanford, the theoretical work of Nagarajan, another well known worker in the field of micelles, supported the shapes proposed by Israelachvili et al. Nevertheless, evidence of toroidal micelles is yet to be reported.

Despite the lack of experimental evidence for the shapes predicted by Israelachvili et al. the proposed shapes are actually part of a much more extensive theory of micellisation which has sound geometric grounding and thus deserves further attention. One of the most significant contributions of the theory was the introduction of the concept of packing parameter which enables the prediction of general micellar shapes from just three geometric quantities; $R$ and $v$, the micellar core radius and volume, respectively and $a_0$, the optimal head group area. $R$ and $v$ are self-explanatory but $a_0$ is a newly introduced quantity and is equal to the value of head group area at which the change in the free energy of the surfactant with head group area is minimised. A key assumption in this theory is that $a_0$ is constant at all places on the micellar core interface. Indeed, it is because ellipsoidal shapes require $a_0$ to vary across the surface of the micelles that they were deemed to be energetically unfavourable.

To continue, we first consider a spherical micelle. From simple geometric arguments the mean aggregation number $M$ can be calculated by,
\[ M = \frac{4\pi R^2}{a_0} = \frac{4\pi R^3}{3v} \quad (2.7) \]

from which it follows that,

\[ R = \frac{3v}{a_0} \quad (2.8) \]

Then, by replacing \( R \) with \( l_{\text{max}} \) (the fully extended chain length) the boundary condition under which spherical micelles can exist is determined as

\[ p = \frac{v}{a_0 l_{\text{max}}} < \frac{1}{3} \quad (2.9) \]

where \( p \) is the packing parameter.

Thus, from simple geometry (and the assumption that \( a_0 \) is constant across the whole surface of the micelle) it has been possible to calculate some boundary conditions for the formation of spherical micelles i.e. when \( p < 1/3 \). Using a similar derivation but for cylindrical shapes it was found that cylindrical micelles would form when \( 1/3 < p < 1/2 \) and finally bilayers form when \( 1/2 < p < 1 \). The globular and toroidal micelles were thought to be the most stable shapes arising in the transition from spherical to cylindrical micelles. It is important to stress that the model does not accommodate for ellipsoidal shapes so it is not true to say that the cylindrical micelles predicted in the theory of Israelachvili et al. are equivalent to the prolate ellipsoids predicted by Tanford’s model. Instead the ellipsoidal shapes in Tanford’s model are analogous to the ‘globular’ micelles arising between the spherical and cylindrical regimes in the model of Israelachvili et al.

An interesting note to consider is that the authors suggest that the packing parameter is only really valid for aggregates with relatively low aggregation numbers where it is believed the assumption that \( a \approx a_0 \) is most
likely to be valid. For larger aggregates, it is said that micellar growth can occur via energetically unfavourable processes. A key example of energetically unfavourable growth is in the formation of sphero-cylindrical micelles which are composed of a central cylinder with hemispherical caps. In this case \( p > 1/3 \) for the cylindrical part whereas for the hemispherical caps \( p = 1/3 \) so that \( a > a_0 \) in the end caps. Thus, while there are useful aspects in the theory as a whole, there also remain elements of uncertainty in it. Tanford’s theory of ellipsoidal micelles, on the other hand, is far more consistent with experimental data. Accordingly, we assume ellipsoidal micelles are possible in the interpretation of our data.

### 2.2.3 Population coexistence

Micellar structures are dynamic, meaning that rather than having a precise shape and size they tend to exhibit a distribution about some mean value. The mean value, in turn, is determined by the minimisation of the free energy of the micelles. This being the case, one can ask an interesting question: what would happen to the shapes of micelles if the free energies of two (or more) completely different shapes were equal? The logical answer would be that multiple micellar shapes would coexist in solution, but neither Israelachvili et al. nor Tanford’s theories explicitly mention micellar shape coexistence. One could infer that the packing parameter concept would not support the coexistence of multiple micelles since it is assumed that \( a_0 \) is constant across the whole micellar interface and the likelihood of two different micellar shapes exhibiting the same \( a_0 \) values is very small. On the other hand, the authors did also propose the existence of sphero-cylindrical micelles in which the area per head group varies across the micelle. So the possibility of varying head group area was not rejected outright.
Some of the earliest data indicating the coexistence of micellar shapes was published by Mukerjee and Yang but their findings were based on cmc measurements. Moreover, the system they studied was a binary mixture of hydrocarbon and fluorocarbon surfactants. It was explained that the mixture of these two surfactant types led to the formation of two types of micelles due to the high degree of non-ideality of mixing between the two surfactant types. Thus, although the results indicated that multiple micellar shapes were possible, the thermodynamics of the system was also probably quite different to that of a pure, single surfactant system.

In recent years, the emergence of more powerful experimental techniques has enabled more precise probing of micellar systems. Techniques such as small angle X-ray and neutron scattering (SAXS and SANS), dynamic light scattering (DLS) and cryo-TEM have all been particularly revealing. Using these techniques workers have been able to show that coexistence of multiple micellar shapes does in fact occur even for single surfactant systems. For example, Majhi et al. found coexistence of spherical and rod-like micelles in solutions of dimethyldodecylamine oxide in a particular pH range using DLS. Glatter et al., on the other hand, studied non-ionic C\textsubscript{12}E\textsubscript{6} micelles using SANS and concluded that globular and short rod-like micelles coexisted in certain conditions. Similarly, Baverback et al. concluded from SANS and SAXS experiments that solutions of C\textsubscript{12}E\textsubscript{6} micelles consisted of spherical and cylindrical micelles in coexistence. Perhaps the most convincing evidence of coexistence of multiple micellar populations was provided by Bernheim-Groswasser et al. in the form of cryo-TEM images of non-ionic C\textsubscript{12}E\textsubscript{5} micelles where the images clearly show spherical and long worm-like micelles in coexistence.

In addition to the experimental evidence which indicates the coexistence of multiple micellar populations, recent computer simulations also predict this
phenomenon. In particular, the simulations produced by the self consistent mean-field theory (SCMFT) show that coexistence of multiple micellar populations is common and should be expected for all types of surfactants. This is bold claim and still requires support from more experimental data, but SCMFT has been able to successfully predict the cmc’s of various $C_mE_n$ surfactants\textsuperscript{47} suggesting that the theory is fairly reliable.

The combination of experimental and simulation results demonstrates that coexistence of multiple micellar shapes does occur and so the possibility of multiple micellar shapes must not be overlooked in the analysis of experimental data.

### 2.3 Thermodynamics of Micellisation

The key concepts that have been revealed from the discussion so far are that:

- micelles begin to form spontaneously at some fixed concentration (cmc),
- above the cmc, micelles are in equilibrium with surfactants in the bulk (which are at a concentration equal to the cmc),
- the aggregation process is entropically driven from the unfavourable interactions between surfactant tails and water and
- micelles have an optimal size depending on the surfactant structure.

These points are not only substantiated by thermodynamic analysis but their origins are also more clearly highlighted.

We start by noting that micelles are equilibrium structures, meaning that in a micellar solution all micelles of different sizes and single surfactant monomers are in equilibrium. Accordingly, the free energies or chemical potentials of all the aggregates must be equal and can thus be expressed as\textsuperscript{48}

$$\mu = \mu_1^o + k_BT \ln X_1 = \mu_2^o + \frac{1}{2} k_BT \ln \frac{X_2}{2} = \mu_3^o + \frac{1}{3} k_BT \ln \frac{X_3}{3} = \ldots$$  \hspace{1cm} (2.10)
where \( k_B \) is the Boltzmann constant, \( T \) is the temperature of the system, \( \mu_m^0 \) is the standard chemical potential of a monomer in a micelle of aggregation number \( m \) and \( X_m' \) is the activity of the micelles with aggregation number \( m \) which can be expressed as \( X_m' = X_m f_m \) where \( X_m \) is the mole fraction of surfactants and \( f_m \) is the activity coefficient of the micelles. Eqn. (2.10) can be simplified to,

\[
\mu_m = \mu_m^0 + \frac{k_B T}{m} \ln \frac{X_m'}{m} = \text{constant} \tag{2.11}
\]

The first term in Eqn. 2.11 represents the free energy of a surfactant in a micelle and the free energy of its interactions with other surfactants in the micelle. The second term is a statistical contribution to the chemical potential arising from the entropy of mixing a micelle with water and has the general form \( k_B T \ln(X_m) \). The \( 1/m \) factor converts this to the contribution per monomer.

If the micelle concentration is sufficiently low it is possible to neglect non-ideality of micelle-micelle interactions so that \( f_m = 1 \) and \( X_m' = X_m \) for \( m > 1 \). However, since the concentration of monomers is much higher (than that of micelles) it is not possible to neglect the possibility of non-ideality of monomer-monomer interactions so that a micellar system can be described by,

\[
\mu_m^0 - \mu_i^0 = k_B T \ln X_1 + k_B T \ln f_i - \frac{k_B T}{m} \ln \frac{X_m}{m} \tag{2.12}
\]

where \( f_i \) is the monomer-monomer activity coefficient and has been separated from \( X_1' \) for convenience.

Eqn. (2.11) is a fundamental equation describing a surfactant system and can also be derived using the mass action model which is another popular approach to the thermodynamic analysis of micellisation. In this model
micelles and monomers are assumed to be in association-dissociation equilibrium as illustrated in Figure 2.5.

Micelles, $M$, are considered to be formed from $m$ monomers, $S$, according to

$$mS \xleftrightarrow{k_1 \quad k_m} M,$$  \hspace{1cm} (2.13)

where $k_1$ and $k_m$ are the association and dissociation rate constants, respectively. Accordingly, the rates of association and dissociation can be given by,

$$\text{rate of association} = k_1 (X_1)^m,$$  \hspace{1cm} (2.14)

$$\text{rate of dissociation} = k_m [M] = k_m (X_m / m).$$  \hspace{1cm} (2.15)

Figure 2.5 – Cartoon illustration of mass action model. Monomers are in dynamic equilibrium with micelles of all sizes.
Finally, inserting the standard Arrhenius equation for the rate constants, \( k = e^{-m\mu_0/kT} \), the equilibrium constant, \( K \), becomes

\[
K = k_1(X_1)^m / k_2(X_m/m) = \left( \frac{m(X_1)^m}{X_m} \right) e^{-m\mu_0/kT}.
\]  (2.16)

With some simple manipulation it is found that equations (2.11) and (2.16) are essentially the same and can be more conveniently expressed as

\[
X_m = m(X_1 e^{-\mu_0/kT})^m.
\]  (2.17)

To fully define a surfactant system we have one final equation for the total volume fraction of surfactant, \( X_{tot} \),

\[
X_{tot} = X_1 + \sum_{m=2}^{\infty} X_m \leq 1.
\]  (2.18)

It is worth mentioning that the lower limit of the summation term in Eqn. (2.18) \( m = 2 \) is just a formal limit and in practice \( X_m \) will not contribute to \( X_{tot} \) significantly until \( m \) is much larger than 2.

Eqn. (2.17) is an important result as it outlines the size distribution of micelles. Additionally, it can reveal some of the general properties of a surfactant system. For example, it is seen that when there is no difference between the chemical potentials of the solvated and aggregated monomers i.e. \( \mu_0 = \mu_m \) the expression reduces to,

\[
X_m = m(X_1)^m
\]  (2.19)

indicating that in this scenario most of the surfactant molecules will be in the single monomer state. When \( \mu_m < \mu_0 \), on the other hand, Eqn. (2.17) tells us that micelles will form and that their size and polydispersity will depend on the
functional relationship between $\mu_m^o$ and $m$. Moreover, it can be seen that the optimal size of a micelle, $m^*$, will be at the value of $m$ when
\[ \frac{\partial X_m}{\partial m} = 0 \]  
(2.20)

Another important feature of Eqn. (2.17) is its relation to the cmc. Consider, for example, the situation when the concentration of surfactant is low enough that $X_m e^{[\mu_n^o - \mu_m^o / kT]} \ll 1$. In this case, we have $X_1 > X_2 > X_3 > \ldots$ meaning that most surfactant molecules exist as individual monomers. However, since $X_m$ cannot exceed unity it is clear that when $X_1$ approaches $e^{[\mu_n^o - \mu_m^o / kT]}$ it can no longer increase. Thus, at this critical concentration further addition of surfactant must lead to the formation of aggregates. This concentration, therefore, corresponds to the critical micellar concentration and can be expressed as
\[ cmc \approx e^{[\mu_n^o - \mu_m^o / kT]} \]  
(2.21)

### 2.3.1 Molecular-Thermodynamic Approach

Eqn. (2.17) is an explicit distribution function of micellar size. Its application requires knowledge of the relationship between $\mu_m^o$ and $m$. A number of workers have been able to derive approximations for this relationship which has helped to provide essential qualitative insights into micellisation. For example, Nagarajan and Ruckenstein provided a comprehensive molecular-thermodynamic approach which enabled the prediction of a number of features of micellisation.\textsuperscript{49} Zoeller et al., on the other hand, provided a statistical-thermodynamic framework to model and predict micellisation of non-ionic micelles by utilising the McMillan-Mayer theory of multi-compartment solutions.\textsuperscript{50} Some theories have also allowed quantitative
predictions of micellar properties. The molecular-thermodynamic theory of Puvvada and Blanckschtein is an example of such a theory. It allows for the respective influences on micellar properties of both the head and tail groups to be predicted, making it particularly useful for understanding micellisation. As a result, we cover the core concepts of the approach in this section. The notation from the original study has been preserved.

The general basis of the theory is that micellisation can be “visualised” as a multi-step process for which the contribution to the free energy of micellisation, $g_{\text{mic}}$, from each step can be evaluated. Since $g_{\text{mic}}$ is defined as the change in free energy when transferring a solvated surfactant monomer into a micelle of size, $m$, semi-minor radius, $l_c$, and shape, $sh$, evaluation of the contributions to $g_{\text{mic}}$ with respect to $l_c$ and $sh$ allows for the general properties of the micelles to be predicted. From the above discussion we can say that $g_{\text{mic}}(m,l_c,sh) = \mu_m^0 - \mu_i^0$. Thus, this approach shows that in addition to an optimal aggregation number (see Eqn. (2.20)) a micelle will also have optimal dimensions, $l_c^*$, and shape, $sh^*$.

The route for a non-ionic surfactant to go from being a single monomer in water to an aggregated monomer in a micelle is illustrated in Figure 2.6. Step 1 is purely conceptual and thus makes no contribution to $g_{\text{mic}}$. The remainder of the steps do contribute to $g_{\text{mic}}$ and are discussed in more detail below. Steps 2, 3 and 4 all relate to the surfactant tail and are, therefore, referred to as the ‘tail effects’. Step 5 corresponds to changes of the head group and is thus termed ‘head effects’.

**Tail Effects**

In the conceptual step 1 the head and tail are separated. After this the first contribution to $g_{\text{mic}}$ comes from transferring the surfactant tail from water to hydrocarbon (step 2 Figure 2.6). As mentioned previously this is effectively the
driving force behind micellisation and is thus an attractive force\textsuperscript{iii} termed $g_{w/\text{hc}}$. The contribution is temperature dependent and has the form

$$g_{w/\text{hc}} = h_{w/\text{hc}} - T s_{w/\text{hc}}$$

(2.22)

where $h_{w/\text{hc}}$ and $s_{w/\text{hc}}$ are the enthalpic and entropic contributions, respectively.

Next, the hydrocarbon-water interface is to be formed (step 3, Figure 2.6). Remembering that there are no head groups at this stage to shield the hydrocarbon droplet from water this contribution, $g_{\sigma}^i$, is repulsive. It is necessary to include the curvature effect in this contribution and, thus, the free energy per monomer can be given by

$$g_{\sigma}^i = \sigma a$$

(2.23)

\textbf{Figure 2.6 – Conceptual route for transferring a free surfactant monomer into a micelle as outlined by Puvvada and Blanckschtein}

\textsuperscript{iii} Attractive in the sense that it causes monomers to be attracted to each other
where $\sigma$ is the interfacial energy per unit area and $a = S v / l_c$ is the interfacial area per monomer (head group area). $S$ is the shape factor which introduces the dependency of the head group area on the micellar shape with $S = 3$ for spheres, 2 for cylinders and 1 for disks/bilayers. The different values for $S$ indicate the energetic cost of forming different shapes. Interestingly, spheres make the largest contribution to free energy here, meaning that they are the least favourable shape. Bilayers, on the other hand, are most favoured. $v$ is the volume of the surfactant tail which is given by Eqn. (2.6) and $l_c$ is the semi-minor axis of the micellar core.

In addition to the dependence of $a$ on micellar shape, the curvature dependence of $\sigma$ is also accounted for as the Gibbs-Tolman-Koenig-Buff equation is used

$$
\sigma = \sigma_0 \left[ 1 - (S - 1) \frac{\delta}{l_c} \right] \quad (2.24)
$$

where $\sigma_0$ is the interfacial tension of a planar hydrocarbon-water interface, $\delta$ is the Tolman distance and $S$ and $l_c$ are the shape factor and micellar core semi-minor axis, respectively, as above. We see the influence of $S$ again here, spherical micelles give rise to the largest interfacial tension and as one would expect bilayers have zero surface tension. Putting Eqn. (2.24) into (2.23) reveals the order of shapes that are favoured as bilayers > cylinders > spheres.

The final step with regards to the tail is to anchor the tail at the hydrocarbon-water interface (step 4, Figure 2.6). This effectively constrains one end of the chain (at the interface) resulting in a loss of some of its conformational degrees of freedom. This contribution $g_{hc/mic}$ is, therefore, also repulsive. The loss of conformational free energy can depend strongly on the shape of the micelle and Puvvada and Blanckschtein follow the work of Ben-Shaul et al. and Greun who use the single-chain mean-field model to evaluate conformational dependency of the energy of hydrocarbon chains. This model
is limited to regular shapes, so the evaluation is performed for spheres, infinite-cylinders and infinite-disks and the results are discussed below.

**Head Effects**

The first head effect is to re-attach the head groups to the tails. As the tails have formed a hydrocarbon droplet in steps 2-4, attachment of the head groups essentially screens some of the droplet from the solvent (step 5a, Figure 2.6). The screened area $g^h_\sigma$ is given by,

$$g^h_\sigma = \sigma a_0$$

(2.25)

where $\sigma$ is given by Eqn. (2.24) and $a_0$ is the chemical bond area between the head and tail groups. $a_0$ corresponds to the interfacial area per monomer screened by the head group. In effect, this screening simply reduces the total interfacial area of the hydrocarbon chain in contact with solvent, so Eqns. (2.23) and (2.25) can be combined to give the following expression for the total interfacial free energy per monomer,

$$g_\sigma = g'_\sigma - g^h_\sigma = \sigma (a-a_0)$$

(2.26)

Upon re-attaching the heads, it is finally necessary to account for the steric interactions between head groups (step 5b, Figure 2.6). These are accounted for by treating the head groups at the core surface as an ideal-localised monolayer of head groups which reflects the physical attachment of the head groups to the tails in the core. By doing this, the steric contribution $g_{st}$ can be expressed as,

$$g_{st} = -kT \ln(1-a_h/a)$$

(2.27)

---

Note: the definition of $a_0$ here is not the same as the optimal head group area discussed in the previous section.
where $a_h$ is the average cross-sectional area of a head group calculated as $v_h/l_h$. $v_h$ and $l_h$ are the volume and end-to-end distance of the head group, respectively. While $v_h$ can be calculated from molecular volumes, $l_h$ depends on the conformation of the head group. For alkyl ethoxylate surfactants, the head groups have been shown to obey standard polymer scaling laws for even very short head groups, so $l_h$ can be calculated using simple polymer relations.

**Evaluating $g_{mic}$**

Having found expressions for each of the contributions to the free energy of micellisation Puvvada and Blankshtein next go on to numerically evaluate all the expressions. Then, $g_{mic}$ is minimised with respect to $l_c$ to find the optimal micellar size $l^*_c$ for a particular shape. The optimal shape $sh^*$ is then found by minimising $g_{mic}^*(sh)$ with respect to $sh$. Since the evaluation of $g_{nc/mic}$ is limited to the three regular shapes, spheres, infinite-cylinders and infinite-bilayers, however, only these three shapes were considered. This being said, the molecular-thermodynamic expressions do not account for contributions from the entropy of mixing which favours the formation of a large number of small, finite sized aggregates than a small number of large aggregates. Thus, if the evaluation of $g_{mic}$ suggests infinite-cylinders or bilayers are the optimal shape, the micellar solution will realistically consist of finite sized cylindrical or disk-like micelles, respectively.

In total, the model consists of three molecular parameters $n_c, \delta$ and $a_h$. $n_c$ is a known property of the hydrocarbon chain while $\delta$ and $a_h$ can be evaluated as discussed above. Using typical values for the parameters and evaluating all the contributions for various surfactants some interesting results were revealed. Firstly, it was found that for all the surfactants considered $g_{mic}^*(disk) = \infty$ i.e. the free-energy contribution from steric interactions is infinitely large for disk-like shapes, indicating that the disk-like shape is
extremely unfavourable. For spheres and infinite-cylinders the following key observations were made:

- The only attractive contribution to $g_{\text{mic}}^*$ was from $g_{\text{w/hc}}^*$ (where the * denotes optimal values) and this also happened to be the contribution with greatest magnitude. The other contributions were repulsive and their magnitudes reduced in the following order $g_{\sigma}^* > g_{\text{hc/mic}}^* > g_{st}^*$ for both shapes. That $g_{\text{w/hc}}^*$ is the largest contributor to free energy of micellisation (~6 times larger than $g_{\sigma}^*$) is entirely consistent with the phenomenological theory discussed in the previous section. It clearly highlights the significance of the unfavourable hydrocarbon-water interactions.

- In general, there is an increase in $g_{st}^*$ with $a_h$ and the increase is more significant for cylindrical shapes. This suggests that surfactants with larger head groups will favour the formation of spherical micelles over cylindrical shapes.

- For $C_{12}E_4$ $g_{\text{mic}}^*(\text{cylinder}) < g_{\text{mic}}^*(\text{sphere})$; $C_{12}E_6$ $g_{\text{mic}}^*(\text{cylinder}) \approx g_{\text{mic}}^*(\text{sphere})$; $C_{12}E_8$ $g_{\text{mic}}^*(\text{cylinder}) < g_{\text{mic}}^*(\text{sphere})$. Thus, there is a shape transition as the head group grows, which is due to the change in $g_{st}^*$ from (2).

- The optimal micellar core radius $l_c^*$ is larger for spheres than cylinders and decreases with $a_h$. This means that larger head groups lead to the formation of smaller micelles.

These findings certainly help to understand micellisation more clearly and the points above demonstrate some key features of micelles. This being said, the practical use of theoretical discussions is very limited in micellar studies. It does not enable the sizes or the shapes of micelles to be easily predicted. This issue thus limits applications of micelles. This is why
experimental studies on micelles are extremely important for advancing our understanding of micellar science. With the powerful experimental techniques that are available today we are able to probe micelles in more detail than ever before, and despite the extensive work that has been conducted in the past there is still scope for further work.

2.4 Micellar Solubilisation

In the previous section, it was shown that the tendency of micelles to form a core-shell structure was due to the amphiphilic nature of surfactants. We now turn our attention to one of the key consequences of this core-shell structure which also happens to be the most useful property of micelles, that is their ability to solubilise hydrophobic substances while remaining thermodynamically stable in aqueous solution.

2.4.1 Basic Thermodynamic Principles

The solubilisation of hydrophobic and hydrophilic substances in micelles arises due to the presence of different regions with varying chemical nature within the micelle. In the standard core-shell micelle, for example, the core, shell and palisade layer all have unique characteristics. The core consists exclusively of hydrocarbon tails and is thus extremely hydrophobic. The shell, on the other hand, contains head groups and water, making it hydrophilic. The palisade layer at the interface between the core and shell has properties that depend on the specific structures of the head and tail. Consequently, these three main domains are attractive to non-polar, polar and amphiphilic substances, respectively.

It follows then that solubilisation is a thermodynamic process and in fact the thermodynamic principles governing micellar solubilisation are essentially the same as those governing the dissolution of surfactants.
Therefore, one can follow a similar process to that in Sec. 2.3 to derive the following equation for a surfactant-solubilisate system,

\[ X_m = X_1^m X_1^n e^{\frac{m \mu_1^0 + n \mu_0^s - \mu_{mn}^0}{kT}} \] (2.28)

where \( X_m \) is the mole fraction of surfactant in micelles of aggregation number \( m \), \( n \) is the number of solubilisate molecules in the micelle, \( X_1 \) is the activity of surfactant in the micelle of aggregation number \( m \) and \( X_1' \) is the activity of solubilisate in monomeric form. \( \mu_1^0 \), \( \mu_0^s \) and \( \mu_{mn}^0 \) are the standard chemical potentials of surfactants in monomer form, solubilisates in monomer form and micelles of aggregation number \( m \) containing \( n \) solubilisate molecules. Eqn. (2.28) is the fundamental equation describing the size distribution of micelles in the presence of a solubilisate and is thus the solubilised system analogue of Eqn. (2.17) which was for the pure micellar system.

One could feasibly obtain some quantitative predictions by evaluating Eqn. (2.28) just as evaluation of Eqn. (2.17) led to predictions for the micellisation behaviour of surfactants. However, the process of evaluating Eqn. (2.28) is more involved because the presence of a solubilisate not only affects the basic contributions to the surfactant free energy (outlined in Sec. 2.3.1) but it also introduces new free energy contributions such as the free energy of mixing. Nevertheless, some workers have been able to evaluate the terms and produce predictions. Nagarajan and Ruckenstein, for example, derived a predictive model for solubilisation by analysing the free energy contributions. Remarkably, their model was able to predict, with reasonable accuracy, the molar solubilisation ratios (MSR, ratio of solubilisate to surfactant in a solution) of simple alkanes and even cyclohexane. However, the model was less successful in predicting the solubilisation of aromatic compounds such as benzene and toluene. They claimed that the reason for this was that the model assumed all of the solubilisate was solubilised in the core of
the micelle whereas the aromatic substances were likely to be distributed throughout the core and the shell due to their polar nature. Consequently, their model would underestimate the solubilisation ratio. Although this justification sounds reasonable, Fendler et al. showed that acetophenone and benzophenone – two aromatic compounds that are more polar than benzene and toluene – solubilised predominantly in the cores of non-ionic C₇E₉ and C₉E₆ micelles.52 Thus, while there may well have been some benzene and toluene in the shells of the micelles it seems unlikely that this was the cause for the disagreement between the model predictions and experimental values. An alternative explanation is simply that the model was not detailed enough to predict the solubilisation of aromatic substances.

Despite the shortcomings of the Nagarajan and Ruckenstein model their study clearly highlighted that micellar solubilisation is a thermodynamically complex process. It is perhaps due to this complex nature that so few theoretical thermodynamic studies have been performed. But regardless of the reasons given already, the simple fact is that theoretical discussions are not particularly useful in predicting the solubilisation of complex molecules such as pesticides. Experimental studies, on the other hand, have been able to provide much more valuable insight. In particular they have been able to illustrate some of the key influences of solubilisation on micelles. These are discussed below.

2.4.2 Influence on Micellar Properties

Comparison of Eqns. (2.17) and (2.28) indicates that the presence of solubilisates in micellar solution will influence the size distribution of micelles. What is not shown in the equations, however, is that solubilisates can also influence the cloud point of a surfactant. Details of these effects have been obtained from experimental studies.
Cloud Point

The cloud point (also referred to as the lower consolute temperature) is the temperature at which the isotropic micellar solution undergoes a phase transition and the solution becomes cloudy. The exact state of the solution just above the cloud point depends on the particular surfactant but Mitchell et al. have described the state for C_mE_n surfactants as co-existing of two phases, a water phase containing monomer at a concentration of the cmc (or just below cmc) and a micelle rich phase. In other words, above the cloud point the micelles are no longer homogeneously dispersed.

While all surfactants exhibit a cloud point, the property is commonly associated with non-ionic C_mE_n surfactants because these surfactants tend to exhibit lower cloud points than ionic surfactants. The reason for this is that the ether oxygen in the ethoxylate head group has a high affinity to water and, therefore, needs to remain hydrated. Raising the temperature of the solution, however, causes the shell to dehydrate resulting in a relatively low cloud point temperature.

One can see from the above description that if the micelle was to be dehydrated by some other means, for example, by adding a dehydrating substance to the solution then the cloud point would be depressed. Conversely, substances that promote shell hydration will increase the cloud point. In the context of this study this is an important feature to remember since the cloud point essentially limits the maximum stable temperature of the micellar solution. Thus, if a solubilisate was to significantly reduce the cloud point it could adversely affect the performance of the formulation. In the agrochemical industry products are often exposed to a wide range of temperatures, so it is necessary to ensure that the formulation remains stable throughout the temperature range. In order to ensure this, knowledge of how substances influence cloud point is required.
Size, Shape and Structure

The influence of a solubilisate on the structural characteristics of micelles is of interest for both practical and fundamental reasons. In agrochemicals, the size of micelles is important because it has been reported that the uptake of substances by foliage is inversely proportional to their molecular weight.⁵⁶ Thus, if micelles are to grow too large after solubilisation of AIs it may affect the efficacy of the pesticide formulation. From a fundamental point-of-view it is of interest to not only understand what influence solubilisates have on micelles but also how and why they administer their influence.

From the thermodynamic analysis of micellisation it was seen that the sizes and shapes of micelles are coupled and depend on the specific interactions of the head and tail groups with the solvent and one another. This means that the influence of a solubilisate on the physical properties of a micelle will depend on how it influences these interactions. In general, solubilisates do not influence the interactions between the surfactant tail and water, but their presence in the micelle does often affect interactions between surfactant head groups. For example, solubilisation of benzene in \( \text{C}_{16}\text{TABr} \) micelles resulted in micellar growth⁵⁷ due to benzene's weakening effect on the electrostatic repulsion between surfactant head groups. Similarly, \( \text{n-dodecanol} \) was found to cause an increase in the length and diameter of \( \text{C}_{10}\text{E}_5 \) micelles⁵⁸ due to its influence on the interactions between surfactant head groups. Interestingly, the same authors also reported that solubilisation of \( \text{n-dodecane} \) in various \( \text{C}_m\text{E}_n \) micelles caused a reduction in micellar size. But this too was attributed to the influence of \( \text{n-dodecane} \) on head group interactions. In this case, however, the influence of the solubilisate was thought to be so great that it caused the micelles to grow excessively which, in turn, caused them to become unstable and eventually collapse.⁵⁹
The above examples demonstrate that one of the key mechanisms via which solubilisates influence micelles is by affecting the head group interactions. But the latter example also suggests that even solubilisates acting via the same mechanism can cause opposite changes in micellar properties. This reflects the findings of the thermodynamic analysis of solubilisation in demonstrating the complex nature of the solubilisation process. But to further complicate the topic other studies have suggested a number of other mechanisms via which solubilisates can act on micelles. Tornblom et al. showed, for example, that solubilisation of cyclohexane in \( \text{C}_{16}\text{TAB} \) micelles led to a reduction in micellar size.\(^{60}\) This was attributed to the formation of a solubilise rich region in the centre of the micelles which caused instabilities and eventual break-up of the micelles into smaller aggregates - a mechanism which was also predicted from thermodynamic calculations by Nagarajan\(^{61}\). Penfold et al., on the other hand, proposed yet another influencing mechanism to describe the reduction in aggregation number of \( \text{C}_{12}\text{E}_{12} \) micelles upon solubilisation of model perfume phenyl ethanol.\(^{40}\) It was claimed that the phenyl ethanol molecules behaved as a co-surfactant and displaced \( \text{C}_{12}\text{E}_{12} \) monomers from the micelles, thus causing a reduction in the overall surfactant aggregation number.

Clearly then, there are numerous ways in which a solubilisate can influence a micelle and predicting the influence using even empirical data is difficult. Accordingly, we propose that a more suitable approach is to try and characterise each of the key influencing mechanisms. This way one could potentially predict the influence of any given solubilisate on a micelle by only identifying the influencing mechanism.
2.4.3 Location of Solubilisate in Micelle

In order to characterise the influencing mechanisms of solubilisates one needs to be able to identify which mechanism a solubilisate acts by. Since influencing mechanisms have not been explicitly studied, however, there is no established method for doing this. Nevertheless, if one studies the literature on solubilisation one finds that the location of the solubilisate is an important factor in determining its influencing mechanism. Thus, a key step in characterising the influencing mechanisms of solubilisates is to determine their location.

As mentioned previously, there are three regions in a micelle in which a solubilisate can exist, the core, shell and palisade layer. Mukerjee was among the first to propose a theoretical model for predicting the location of solubilisates in C\text{m}E\text{n} micelles.\textsuperscript{62} Their model, however, relied on the assumption that the partitioning of the solubilisate between the core and shell is proportional to the equivalent number of alkyl chain moieties and that of ethoxylate groups. While this assumption was suitable for some simple solubilisates Goldenberg et al. found that the Mukerjee model was inconsistent with the experimental observations of solubilisation of insecticides\textsuperscript{63}.

It is now widely accepted that the charge properties and amphipilic character of a solubilisate influence its interaction with surfactant micelles, however, the exact location is thought to be strongly dependent on its hydrophobicity. The more hydrophobic the substance is the deeper it penetrates into micelles. The findings of Fischer et al.\textsuperscript{64} were broadly consistent with this perception. In their study, the hydrophobicity of a number of fragrances was quantified using the octanol-water partitioning coefficient, LogP_{ow} (where higher LogP_{ow} coefficients represent more hydrophobic molecules). It was found that when LogP_{ow} > 3.5 the molecules fully solubilised in the micelles and were located in the core. For intermediate
LogP$_\text{ow}$ values the fragrances were dissolved in the bulk solvent and the micelles. Those molecules in the micelles were generally in the core but near the palisade layer. For low LogP$_\text{ow}$ the fragrances were mostly partitioned in the bulk solvent but a small fraction of molecules in the micelles preferred to be in or near the hydrophilic shell. Thus, according to the current theory a solubilisate’s location in a micelle can be determined by its LogP$_\text{ow}$. 
3 Experimental Techniques

Many different spectroscopic techniques have been used to study micelles in the past including small angle X-ray and neutron scattering (SAXS and SANS), nuclear magnetic resonance (NMR) and UV absorption. SAXS and SANS have been especially useful in studying the shapes and sizes of micelles while NMR and UV have provided key insights into solubilisation, the internal structure of micelles and their hydration. In this study, results from SANS, NMR, UV and dynamic light scattering (DLS) have been combined to develop a detailed understanding of pure and solubilised $C_mE_n$ micelle systems. It has been possible to elucidate the effects of surfactant structure and pesticide solubilisation on the shape, size and structure of micelles. In this chapter we introduce each of the experimental techniques and explore some of their fundamental concepts.

3.1 Small Angle Neutron Scattering (SANS)

SANS is a scattering technique that exploits the interaction between neutrons and atomic nuclei to reveal information about the size and shape of molecules. The typical length scales probed in SANS experiments is $0.5 - 100$ nm which is ideal for soft matter systems such as colloids and micelles. While it is possible to probe a wider range of sizes with SAXS (around $0.1 - 2500$ nm) X-ray scattering is also much more likely to cause radiation and/or heat damage. This makes SANS a favourable technique especially for the study of biological systems. Indeed one could use light scattering (LS) since this is also a non-destructive technique but the length scales probed using visible light are generally much larger at around $5 - 25000$ nm. Thus, SANS offers a convenient balance between the high and low energy scattering techniques (SAXS and LS,
respectively) for how much detail that can be extracted about a system and the associated risk of damaging a sample.

There are a couple of problems with SANS, however, such as:

- Limited availability of neutron sources – Neutrons are produced either by nuclear fission in a reactor or by spallation using accelerated protons in a synchrotron. In both cases large purpose built facilities are required which are costly to run. Consequently, there are only around 25 neutron facilities around the world so competition for neutron beam time can be quite high. This means SANS is not particularly accessible. In comparison to light scattering which is a lab based technique, for example, SANS is a difficult and expensive technique.

- Modelling data – Provided one is able to get access to neutron beam time and perform experiments it is then necessary to analyse the scattering data. This, however, is not an easy process. Despite the extensive use of SANS for studying soft matter systems, it is generally difficult to undertake data analysis. Additionally, there is very little software available to help fit data. The software that is available is generally poorly documented and not very user-friendly. Therefore, most workers tend to analyse data manually at the expense of it being more time-consuming and wrongly interpreted.

### 3.1.1 SANS Apparatus

Neutrons can be generated via two main methods, either by neutron fission or by spallation from a metal target. The former requires a fission reactor while the latter uses a synchrotron to accelerate protons to around 80-90% the speed of light before bombarding into the metal target. Both methods generate very high energy neutrons so moderators are used to slow the neutrons down
before they can be used. This process is particularly important for SANS because the reduction in speed effectively increases the neutron wavelength which, in turn, enables the study of smaller particles.

The path of the neutrons after leaving the moderator depends on the neutron source. Generally, for reactor sources, the neutrons are passed through a neutron bandpass filter to select a narrow wavelength range while for spallation sources the neutrons are left as a pulse containing a broad range of wavelengths. The significance of this will become clearer below.

Next, the neutron beam (or pulse) will pass through a collimator and a low efficiency detector to monitor the input intensity before arriving at the sample. After scattering off a sample the intensity of neutrons are finally measured by a bank of high efficiency 2-dimensional detectors.

In general, all scattering techniques require the same core components; a source, a sample area and a detector. But the unique thing about SANS apparatus is the sheer size. The total distance travelled by a neutron from the point it is generated to hitting the detector can be as high as 200m. While this is impressive in itself it is even more striking that only a small portion of the total path length is not under vacuum. This is necessary because there is approximately 10% loss in neutron flux for each meter travelled in air. Overall, neutron facilities are incredibly complex and hugely impressive.

3.1.2 Scattering Theory

In general, the wavelength of neutrons (~0.01 – 3nm) is a number of orders of magnitude greater than the size of atomic nuclei. This means the atomic nuclei behave as point scatterers and scatter neutrons elastically in all directions as described by the Rayleigh-Debye-Gans theory. Consequently, there is no angular dependence introduced by the interaction of a neutron with a nucleus. However, diffraction effects between different scattered waves do introduce an
angular dependence and since these effects are dependent on the specific arrangement of scatterers it is possible to determine the shape, size and structure of a scattering particle by analysing the scattering profile.

Let us first consider the scattering of a beam of neutrons from a single nucleus fixed in space as shown in Figure 3.1. Due to the wave-particle duality of neutrons the incident collimated neutron beam can be represented by the following wavefunction,

\[ \Psi_i = e^{ikz} \]  

where \( z \) is the distance separating the neutron and nucleus and \( k_i = 2\pi/\lambda \) is the wave number. The neutrons are scattered spherically since the nucleus diameter is of the order of \( 10^{-15}\text{m} \) and the neutron wavelength is typically of the order of \( 10^{-10}\text{m} \). Thus, the scattered wave can be represented by the wavefunction,
\[ \Psi_x = \frac{-b}{r} e^{ikr} \]  

(3.2)

where \( b \) is the nuclear scattering length of the nucleus and represents the interaction of a neutron with the nucleus. The scattering length is an intrinsic property of a nucleus and can be understood as the neutron analogue of refractive index in optics. It is, therefore, a very important property for neutron scattering. In general, \( b \) is a complex number but the imaginary part only becomes significant for nuclei with a high absorption coefficient, \( s_{abs} \). Since most nuclei of interest have a low absorption coefficient (see Table 3.1) \( b \) can be treated as a real quantity. The value of \( b \) varies non-linearly with atomic number by virtue of the fact that the neutron-nucleus interaction is governed by the strong force. Indeed the nature of the interaction also means different isotopes of the same element also have strongly varying scattering lengths. This non-linear variation is in fact an important feature of SANS and gives rise to one of the key advantages of SANS over SAXS (and other scattering techniques); substances can be easily labelled by substituting particular

<table>
<thead>
<tr>
<th>Atomic nucleus</th>
<th>( b \times 10^{-15} \text{m} )</th>
<th>( s_{abs} ) (barns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^1 \text{H} )</td>
<td>-3.741</td>
<td>0.3</td>
</tr>
<tr>
<td>( ^2 \text{D} )</td>
<td>+6.671</td>
<td>0.0</td>
</tr>
<tr>
<td>C</td>
<td>+6.646</td>
<td>0.0</td>
</tr>
<tr>
<td>N</td>
<td>+9.362</td>
<td>1.9</td>
</tr>
<tr>
<td>O</td>
<td>+5.803</td>
<td>0.0</td>
</tr>
<tr>
<td>Cl</td>
<td>+9.577</td>
<td>33.5</td>
</tr>
</tbody>
</table>
elements with isotopes. In X-ray scattering, labelling is much more difficult since X-ray scattering is an electronic interaction and thus requires heavy atom labels which can drastically change the properties of a sample. Isotopic substitution, on the other hand, does not affect the sample structure. The most common substitution in SANS is the replacement of $^1\text{H}$ atoms (hydrogen) with $^2\text{D}$ (deuterium). The scattering lengths and absorption coefficients of some common nuclei are given in Table 3.1.

Eqn. (3.2) describes the scattering from a single nucleus but for a collection of nuclei (e.g. a single molecule) the scattered wave becomes,

$$\Psi_s = -\sum_i \left( \frac{b_i}{r_i} \right) e^{i k_i r} e^{i q r}$$

(3.3)

where $q = k_i - k_f$ is the scattering vector and $k_i$ and $k_f$ are the wavevectors of the incident and scattered neutrons. From simple geometry it is found that $q$ is given by,

$$q = |q| = \frac{4\pi}{\lambda} \sin \left( \frac{q}{2} \right)$$

(3.4)

where $\theta$ is the scattered angle. By inserting Eqn. (3.4) into Bragg’s Law of Diffraction,

$$\lambda = 2d \sin \left( \frac{\theta}{2} \right)$$

(3.5)

a useful expression is obtained,

$$d = \frac{2\pi}{q}$$

(3.6)

where $d$ is a distance related to the scattering particle. The above equation shows that $q$ is inversely related to distance. Thus, it is preferable to have as big a $q$ range as possible in order to increase the range of measurable particle sizes.
From Eqn. (3.4) it can be seen that one can vary \( q \) by either varying \( \lambda \) or \( \theta \). In other words, to achieve a wide range of measurable sizes the SANS instrument either needs a broadband neutron beam or a wide scattering angle. One can now see how this relates to the discussion on neutron sources above where it was mentioned that spallation sources generally use a broadband neutron pulse whereas fission sources tend to select a single \( \lambda \). Due to the wide \( \lambda \) range in spallation sources the scattering angle is kept constant by fixing the detector position but in fission sources the detector position is varied to achieve a range of scattering angles. Accordingly, these instruments are referred to as 'fixed-geometry' and 'fixed-wavelength' instruments, respectively.

Eqn. (3.3) gave the wavefunction of the scattered neutrons but in practice neutron detectors measure the intensity of scattered neutrons, so we define a new ‘experimental’ parameter which describes the scattering in terms of measurable quantities. The parameter is called the differential cross section and is defined as

\[
\frac{d\sigma}{d\Omega} = \frac{\text{number of neutrons scattered per second into } d\Omega \text{ in direction } \theta, \phi}{\Phi d\Omega}
\]  

(3.7)

where \( \Phi \) is the number of incident neutrons per unit area per second, \( \theta \) and \( \phi \) are the scattering angles from the z and y axes, respectively, and \( d\Omega \) is the solid angle in the direction \( \theta, \phi \).

In effect the differential cross-section is a measure of how “big” the scattering particle appears to a neutron. It is, therefore, related to the scattering length of the scattering particle since this parameter represents the interaction of the neutron with the scatterer. In fact, as the intensity of scattered neutrons is equal to the squared modulus of the wavefunction,\(^{66}\)

\[
I = \left| \sum_i \left( \frac{b_i}{r} \right) e^{i\mathbf{q}\cdot\mathbf{r}} \right|^2
\]  

(3.8)
Eqn. (3.7) becomes, for any given sample,

\[
\frac{d\sigma}{d\Omega}(q) = \frac{1}{N} \left| \sum_i b_i e^{iq \cdot r_i} \right|^2
\]

(3.9)

where \( N \) is the total number of scatterers. Thus, Eqn. (3.9) demonstrates the relationship between the scattering cross-section of a sample and the scattered wavefunction. Importantly, Eqn. (3.9) is also a function of \( q \), the scattered wavevector. The practical significance of the equation is still difficult to understand, however, due to the inclusion of \( b \) which is an atomic property. We, therefore, define a new parameter called the scattering length density, \( \rho \), which relates \( b \) to the bulk properties of a substance via

\[
\rho = \frac{\sum_i b_i}{V}
\]

(3.10)

where \( b_i \) is the scattering length of the \( i \)'th atom and \( V \) is the volume of the \( N \) atoms. Now by substituting Eqn. (3.10) into Eqn. (3.9) we obtain

\[
\frac{d\Sigma}{d\Omega}(q) = \frac{N d\sigma}{V d\Omega}(q) = \frac{1}{V} \left| \int V \rho(r)e^{iq \cdot r} dr \right|^2
\]

(3.11)

where \( \Sigma = \sigma/V \), the macroscopic cross section, has been introduced to indicate that we are now looking at the cross section of a bulk material as opposed to a single particle. In essence Eqn. (3.11) is just a more convenient way of expressing Eqn. (3.9). It is known as the Rayleigh-Gans equation and demonstrates that small angle scattering occurs due to the inhomogeneous variation of scattering length density in a sample. In actual fact Eqn. (3.11) applies to all scattering methods and only the radiation dependent variables are changed.

It is seen on the right side of Eqn. (3.11) that the integral term is a Fourier transform of the scattering length density distribution and to obtain
the scattering cross section the squared modulus of the Fourier transform is taken. As a result, all phase information is lost meaning one cannot retrieve information about the scattering length density distribution by the inverse Fourier transform of the scattering cross-section. This is a problem faced in all scattering techniques due to the fact that detectors only measure amplitude and not phase. Consequently it is known as the ‘phase problem’.

Now let us consider the practical significance of Eqn. (3.11). Imagine a two phase system consisting of incompressible phases with scattering length densities $\rho_1$ and $\rho_2$ such that,

$$V = V_1 + V_2$$  \hspace{1cm} (3.12)

and,

$$\rho(r) = \begin{cases} \rho_1 \text{ in } V_1, \\ \rho_2 \text{ in } V_2. \end{cases}$$  \hspace{1cm} (3.13)

The scattering cross section for such a system can be expressed as,

$$\frac{d\Sigma}{d\Omega} = \frac{1}{V} \left| \int_{V_1} \rho_1 e^{iqr} dr_1 + \int_{V_2} \rho_2 e^{iqr} dr_2 \right|^2$$  \hspace{1cm} (3.14)

$$\frac{d\Sigma}{d\Omega} = \frac{1}{V} \left| \int_{V_1} \rho_1 e^{iqr} dr_1 + \rho_2 \int_V e^{iqr} dr - \int_{V_1} e^{iqr} dr_1 \right|^2$$  \hspace{1cm} (3.15)

and finally,

$$\frac{d\Sigma}{d\Omega} (q) = \frac{1}{V} (\rho_1 - \rho_2)^2 \left| \int_{V_1} e^{iqr} dr_1 \right|^2.$$  \hspace{1cm} (3.16)

Eqn. (3.16) is the general equation for the scattering cross section of any two phase system. Importantly, it tells us that the scattered intensity of neutrons is proportional to the difference in scattering length densities of the two phases (which is also known as the contrast, $\Delta \rho = (\rho_1 - \rho_2)^2$). Since the
contrast accounts for the bulk and atomic properties of the system the integral term must describe the spatial arrangement of the system. Thus, in order to derive structural information from neutron scattering data, it is necessary to analyse the integral term.

### 3.1.3 Data Analysis

In practice there are a number of instrument dependent factors that modulate the scattering cross-section. Therefore, the scattered intensity, $I_s$, is actually given by,\(^6\)

$$I_s(\lambda, q) = I_0(\lambda)\Delta\Omega \eta(\lambda)TV \frac{d\Sigma}{d\Omega}(q)$$ \hspace{1cm} (3.17)

where $I_0$ is the incident intensity, $\Delta\Omega$ is the area of the detector element, $\eta(\lambda)$ is the efficiency of the detector, $T$ and $V$ are the transmission and volume of the sample, respectively and $d\Sigma/d\Omega(q)$ is the scattering cross-section. However, since all of the modulating terms are independent of $q$ they are usually reduced from raw signal by computer software so that the final output essentially represents just the scattering cross-section. This means one can usually analyse the output data directly.

There are two main approaches to analysing the scattering data:

- **Model-independent analysis** which involves directly manipulating the scattering data to reveal useful information. Khayat et al. gave an excellent demonstration of what information can be obtained from SANS data using this approach.\(^5\)

- **Model-dependent analysis** which uses simplified mathematical models to approximate the scattering length density distribution of the sample and thus reveal details of the scattering particles. Hayter and Pendfold
published a detailed introduction to the use of SANS and model independent analysis for the study of micelles.\textsuperscript{68}

Model-independent analysis is particularly useful when one has little knowledge about the structure of the particles being studied. However, a lot of effort is required to derive information and the process can be cumbersome. Moreover, the method cannot provide precise information. Model-dependent analysis, on the other hand, can provide a great amount of detail about a system but at the same time requires some prior knowledge of the system. In general, model-dependent analysis is easier to perform and has been more widely adopted over the years.

\textbf{Model-independent Analysis}

There are two main model-independent methods that are commonly used: Guinier analysis and Porod’s Law. Both were originally developed for the analysis of SAXS data they are also applicable in SANS. Firstly, in the low $q$ region, Guinier proposed that the following approximation can be used to estimate the scattered intensity\textsuperscript{69},

$$I(q) = I_0 e^{-(qR_{scat})^2/3}.$$ (3.18)

Taking the natural logarithm of both sides gives,

$$\ln(I(q)) = \ln(I_0) - \frac{R_{scat}^2}{3} q^2$$ (3.19)

where $R_{scat}$ is the radius of gyration of the scatterer. Thus by plotting $\ln(I(q))$ vs. $q^2$ one can extract the radius of gyration of a scatterer. More useful parameters can then be deduced from $R_{scat}$ if the geometry of the scatterer is known. For example, for spheres $R_{scat}^2 = 3R^2 / 5$ so one can determine the radius, $R$, of the sphere. The condition for the Guinier approximation is that $qR_{scat} \ll 1$. 

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In the high-q region ($q \gg 1/D$, where $D$ is the size of the scatterer) Porod’s law states that $I(q) \propto q^{-4}$. Therefore, one can determine an approximate value of the smallest dimension of a scatterer by identifying the $q$ value at which the above relationship becomes true.

**Model-dependent Analysis**

Model-dependent analysis takes advantage of the fact that for many systems the integral term in Eqn. (3.16) can be separated into two $q$-dependent functions, $P(q)$ and $S(q)$. $P(q)$ is known as the form factor and represents interference of neutrons scattered by different parts of the same scattering particle and thus encapsulates all the information about the size, shape and structure of the scattering particle. $S(q)$, on the other hand, is the structure factor and represents the interference of neutrons scattered from different scattering particles and, therefore, holds information about the interparticle correlations. By using approximate analytical expressions for $P(q)$ and $S(q)$ one can calculate the $q$ dependence of the scattering cross-section i.e. $d\Sigma/d\Omega(q)$. Then, by adjusting various fit parameters in the two expressions for $P(q)$ and $S(q)$ it is possible to fit experimental data and reveal information about the system. Since the forms of the expressions for $P(q)$ and $S(q)$ are dependent on shape one must have an idea of the structure of the system in order to choose an appropriate expression. The general form of the scattering cross-section becomes,

$$\frac{d\Sigma}{d\Omega}(q) = N_p \rho_1 - \rho_2 V_p^2 P(q)S(q)$$  \hspace{1cm} (3.20)

where $N_p$ is the number concentration of scatterers, $\rho_i$ is the scattering length density of the $i^{th}$ component and $V_p$ is the volume of the scattering particle. It is useful to note that $P(q)$ and $S(q)$ are normalised as follows: $P(q \to 0) = 1$, $P(q \to \infty) = 0$ and $S(q \to \infty) = 1$. 


In an isotropic solution $S(q)$ is given by,

$$S(q) = 1 + \frac{4\pi N_p}{q} \int_0^\infty g(r) r^{-1} [r \sin(qr) dr$$  \hspace{1cm} (3.21)$$

where $r$ is the radial distance from the centre of a scattering particle and $g(r)$ is the pair distance distribution function (PDDF) between two separate scattering particles. $g(r)$ is related to the radial distribution function via,

$$G(r) = \frac{4\pi N_p r^2}{V} g(r),$$ \hspace{1cm} (3.22)$$

This shows that one can gain information about the relative positions of the scattering bodies by fitting $S(q)$. In practice, however, this is a difficult procedure, so a more common approach is to use an approximate function for $S(q)$ and fit that to the data. For example, for charged micelles the rescaled mean spherical approximation (RMSA) calculated for a repulsive screened Coulombic potential is often employed.

It can be seen in Eqn. (3.21) that $S(q) \propto N_p$. This is rather convenient as it means that $S(q) \rightarrow 1$ when $N_p$ is small. Thus, if one is not interested in the interparticle interaction one can use a dilute solution so the effects of $S(q)$ become negligible.

Various analytical expressions for different shapes can be found in literature to approximate $P(q)$ but in the study of micelles the most important form factor is that of an ellipsoid since this is believed to be the most common micellar shape. Although no single expression has been derived for the form factor of an ellipsoid one can approximate it by integrating the form factor of a sphere with an orientation dependent radius through $90^\circ$. Thus, for an ellipsoid with semi-axis $(a, a, c)$ the form factor is given by

$$P_{\text{ellipsoid}}(q) = \int_0^{\pi/2} P_{\text{sphere}} qR(a, e, \alpha) \sin \alpha d\alpha$$ \hspace{1cm} (3.23)$$
where $\varepsilon = a/c$ is the eccentricity, $R(a, \varepsilon, \alpha) = a \sin^2 \alpha + \varepsilon^2 \cos^2 \alpha^{1/2}$ is the orientation-dependent radius and,

$$P_{\text{sphere}} = \left[ \frac{3 \sin qR - qR \cos qR}{qR^3} \right]^2.$$  

(3.24)

By inserting the expressions for $P(q)$ and $S(q)$ into Eqn. (3.20) it is possible to model simple single component systems. But generally soft matter systems, including micelles, are more complex and consist of composite structures. Thus some further work is required to model these as shown below.

Consider a dilute solution of non-interacting micelles for which $S(q) = 1$. In this case the scattering cross-section for a single micelle reduces to,

$$\frac{d\sigma}{d\Omega}(q) = V^2_{p}(\rho_1 - \rho_2)^2 P(q).$$  

(3.25)

Remembering $d\sigma/d\Omega(q)$ is proportional to the intensity of neutrons hitting the detector which, in turn, is proportional to the square of the scattering amplitude, $A(q)$, then Eqn. (3.25) can be expressed as,

$$\frac{d\sigma}{d\Omega} = \left[ \sum_{i}^{N} V_{i}(\rho_i - \rho_0)A(q) \right]^2$$  

(3.26)

where $A(q) = P^{1/2}(q)$ has been introduced as the form factor amplitude. Now Eqn. (3.26) can be used to calculate the scattering profile for any composite structure by simply introducing new terms for each component of the total structure that exhibits a unique contrast.

An important point to consider in using model-dependent fitting is that the scattering profile for any given shape or structure is not unique. In other words, it may be possible to fit more than one model to a single set of data. Indeed if a model has many fit parameters it could be used to fit practically
any set of the data. It is, therefore, necessary to verify the fitting results either by contrast variation (explained later) or by some other means such as by using data from another experimental method.

**Core-Shell Model**

Eqn. (3.26) enables us to build a mathematical model for any composite structure by simply summing the contributions from all the components in the structure that either have a unique contrast or a unique form factor. We can perform this process for micelles on the basis of their core-shell structure as discussed in Chapter 2.2. Firstly, the core is composed entirely of hydrocarbon tails, equivalent to a droplet of pure hydrocarbon. This means that it only has a single contrast value and a single form factor and thus can be treated as one component. The shell, on the other hand, is composed of hydrophilic head groups and water so its contrast depends on both the total amount of water it contains and the distribution of the water. While the former can be calculated using simple volume considerations the distribution of the water is more difficult to predict. However, due to the small thickness of the shell it is generally assumed that the water is homogenously mixed in the shell giving the shell a single contrast and form factor too. Overall, the micelle can thus be treated as two separate components, a core and a shell.

For the core a standard form factor expression can be used depending on its shapes but there are no analytical expressions for the form factor of a hollowed shell. Thus, in order to model the shell a new ‘shell form factor’ is constructed simply by deducting a small shape from a larger one. The final scattering cross-section then becomes,

\[
\frac{d\sigma}{d\Omega}(q) = \left[ V_{out} \Delta \rho_{shell} A_{out}(q) - V_{in} \Delta \rho_{shell} A_{in}(q) + V_{in} \Delta \rho_{core} A_{in}(q) \right]^2 \quad (3.27)
\]
\[
\frac{d\sigma}{d\Omega} (q) = [V_{\text{out}} \Delta \rho_{\text{shell}} A_{\text{out}} (q) + (\rho_{\text{core}} - \rho_{\text{shell}}) V_{\text{in}} A_{\text{in}} (q)]^2
\]  

(3.28)

where \( \Delta \rho_{\text{core}} = (\rho_{\text{core}} - \rho_{\text{shell}}) \), \( \Delta \rho_{\text{shell}} = (\rho_{\text{shell}} - \rho_{d2o}) \), \( V_{\text{out}} \) is the volume of the shell, \( V_{\text{in}} \) is the volume of the core and \( A_{\text{in/out}} (q) \) is the amplitude form factor for a chosen shape.

The core-shell model described by Eqn. (3.28) has been used extensively in the study of micelles. In general, ellipsoidal shapes are used since this is the most probable shape of many micelles. While the model has been able to provide very good fits for a number of different micelles there is some disagreement between SANS results and other experimental methods. For example, Penfold et al. suggested that \( \text{C}_{12}\text{E}_6 \), \( \text{C}_{12}\text{E}_8 \) and \( \text{C}_{12}\text{E}_{12} \) micelles were all prolate ellipsoids, whereas Tanford found from intrinsic viscosity and sedimentation velocity measurements that the same micelles formed oblate shapes. It is true that the experimental techniques employed by Tanford are not as reliable as SANS but further evidence is required to support one or the other.

Another possible explanation for the disagreement in the aforementioned results is that the core-shell model used to fit the SANS data does not accurately represent the micelles. Indeed studies on the structure of non-ionic \( \text{C}_m\text{E}_n \) micelles have indicated two areas where the core-shell model might be incorrect. Firstly, it has been shown by Lu et al. using neutron reflection that there is considerable intermixing of the head and tail groups of non-ionic surfactants when they aggregate at the air-liquid interface.\(^{75}\) It is reasonable to assume that similar intermixing occurs at the core-shell interface of micelles but the core-shell model described above does not allow for such mixing. Secondly, it was shown by Podo et al. that a hydration gradient exists in the shells of non-ionic \( \text{C}_m\text{E}_n \) micelles which contradicts the assumption made in the model that the shell is homogenously hydrated.\(^{31}\) While it is not
clear whether these inaccurate assumptions in the core-shell model would have any significant effect on data fitting, it is clear that the model has some flaws. Accordingly, we explored other models that may be suitable for the CmEn micelles.

‘Core-Chain’ Model

A model that looked particularly interesting was the core-chain model developed by Pedersen and Gerstenberg for block co-polymer micelles. In this model the core is still treated as a homogeneous droplet of hydrocarbon as in the core-shell model but the key differences are that there are no assumptions are made about the hydration of the shell and, moreover, intermixing of the head and tail groups at the core-shell interface can be easily accommodated. The model achieves this by treating the ethoxylate (EO) head groups as individual chains as opposed to a homogenously hydrated mixture. Figure 3.2 gives a schematic illustration of how the micelle looks according to the core-chain model.

The derivation of the core-chain model is somewhat different to that of the core-shell model. Rather than constructing a single composite structure using Eqn. (3.26) the core-chain micelle is treated as a combination of individual structures such that the scattering cross-section becomes,
Figure 3.2 – Illustration of micelle as modelled by the core-chain model. Core has a radius, \( R \), and chains in the shell have a radius \( R_g \)

\[
\frac{d\sigma}{d\Omega}(q) = N_{agg} V_c \Delta \rho_c^2 P_c(q) + N_{agg} V_s \Delta \rho_s^2 P_s(q) \\
+ 2N_{agg}^2 (V_c \Delta \rho_c)(V_s \Delta \rho_s) P_{cs}(q) + N_{agg} (N_{agg} - 1)(V_s \Delta \rho_s)^2 P_{ss}(q)
\]  

(3.29)

where \( N_{agg} \) is the aggregation number of the micelle (i.e. number of surfactant monomers in the micelle), \( V_{cls} \) is the volume of the surfactant tail and head chain in the core and shell, respectively, \( \Delta \rho_c = \rho_{core} - \rho_{solvent} \) is the contrast of the micellar core, \( \Delta \rho_s = \rho_{shell} - \rho_{solvent} \) is the contrast of a single surfactant head group in the shell, \( P_c(q) \) is the form factor of the core, \( P_s(q) \) is the form factor of a head group (chain), \( P_{cs}(q) \) is the cross term between the core and a chain and \( P_{ss}(q) \) is the cross term between chains.

The first two terms in Eqn. (3.29) describe the individual components of the micelle while the cross terms account for the interference between them. It is necessary to explicitly include the cross terms because the components are modelled as individual structures. Similar cross-terms also exist upon
expansion of Eqn. (3.28) in the core-shell model but are not explicitly expressed.

While the core-chain model allows for the micelle to be of any shape (by selecting an appropriate expression for \( P_c(q) \)) the head groups are modelled as chains with Gaussian statistics. One might argue that this treatment of the head groups is not accurate for shorter EO chain surfactants, but as previously mentioned, Sarmoria and Blanckschtein showed that even very short EO chains follow polymer scaling laws within experimental error\(^\text{20}\). Therefore, in practice it is reasonable to treat the head groups as Gaussian chains.

For ellipsoidal micelles known form factors can, therefore, be used for all four components. For the core (\( P_c(q) \)) one can use the form factor given by Eqn. (3.23) while for the Gaussian chains the form factor is given by the Debye function\(^\text{77}\)

\[
P_s(q) = \frac{2[e^{-x} - 1 + x]}{x^2}
\]

(3.30)

where \( x = R_g^2 q^2 \) and \( R_g \) is the radius of gyration of the head group and the form factor has been averaged over the ensemble of chain configurations. The derivation of the two cross-terms has been described in detail by Pedersen\(^\text{78}\) but the final expressions are found to be

\[
P_{sc}(q) = A_s(qR_g) \int_0^{\pi/2} A_{sphere}(qR) \frac{\sin q[R + dR_g]}{q[R + dR_g]} \sin \alpha \, d\alpha
\]

(3.31)

\[
P_{cc}(q) = A_c(qR_g) \left[ \frac{\sin q[R + dR_g]}{q[R + dR_g]} \right]^2 \sin \alpha \, d\alpha
\]

(3.32)
where \( A_s(x) = \left[ 1 - e^{-x} \right]/x \) is the amplitude form factor of a single chain, \( A_{\text{sphere}}(x) = P_{\text{sphere}}^{1/2}(x) \) is the form factor amplitude of a sphere (see Table 3.2), \( R = r(\sin^2 \alpha + \varepsilon^2 \cos^2 \alpha)^{1/2} \) is the orientation dependent radius of the core and \( d \) is a constant with a value close to unity. The purpose of introducing \( dR_g \) is to ensure that the chains do not protrude into the core. Importantly, this does not mean that the head and tail groups cannot intermix as the ability to account for intermixing is one of the advantages of this model rather it is used purely for mathematical consistency of the model.

Finally, inserting Eqns. (3.23), (3.30), (3.31) and (3.32) into Eqn. (3.29) gives the \( q \)-dependent scattering cross-section of an ellipsoidal micelle which can be used to fit experimental data in the same way as the core-shell model. In total the core-chain model for ellipsoidal micelles has 3 fit parameters \( r, \varepsilon \) and \( R_g \) which is the same number as the core-shell model in which the fit parameters for the same shape of micelle are \( R_1, R_2 \) and \( \varepsilon \), the semi-minor axes of the core and shell and the eccentricity of the ellipsoid, respectively. Therefore, although the core-chain model is seemingly more complex in nature when it comes to fitting it is as simple as the core-shell model.

**Contrast Variation**

It was seen in Eqn. (3.16) that the scattering cross-section of a scattering particle is proportional to its contrast with the surrounding medium. For a single component particle this means that the contrast simply acts as a scaling factor of the scattering cross-section and is of little practical importance. For composite structures, on the other hand, the contrast plays a more important role. Since each component of the composite structure experiences a different contrast value, varying the contrast of any individual component will result in a non-linear change of the scattering profile. If in the meantime the physical structure of the scattering particle remains unchanged then one should be able
to just adjust the contrast values in Eqn. (3.26) while keeping the form factor constant and be able to achieve good fits to experimental data for both contrasts using the same set of fit parameters. If by changing the contrast value the calculated scattering profile does not fit experimental data for different sample contrasts then this is an indication that the model and/or the fit parameters are incorrect. This process is known as contrast variation.

As previously mentioned, contrast variation is particularly useful in SANS (compared to other scattering techniques) because it can be achieved by isotopically labelling samples. Due to the nature of neutron scattering different isotopes can exhibit significantly different scattering lengths. The most common label used is the substitution of $^1$H for $^2$D. Table 3.2 shows that the scattering lengths of these two isotopes are significantly different yet the isotopic composition of a substance generally has little effect on its physical structure meaning this approach is ideal for the contrast variation process.

### 3.2 Nuclear Magnetic Resonance (NMR)

NMR is a well established experimental technique and is used in almost all areas of science. Over the years several different one and two-dimensional NMR-based techniques have been developed. The simplest and most widely used technique, however, is $^1$H-NMR (referred to as proton NMR). In this 1-D technique, the resonances of molecular protons are measured. Analysis of the positions of the resonance peaks and their shapes can reveal a lot of information about the molecular structure of a substance.

Two-dimensional techniques are able to reveal more precise information about substances and are becoming more popular as NMR instruments become more advanced. A particular technique that is especially useful in the study of micelles is Nuclear Overhauser Effect Spectroscopy (NOESY). This technique can reveal information about the spacial proximity of coupled
protons and can, therefore, be used to study the internal structure of micelles and solubilisation.

In this work both $^1$H-NMR and NOESY NMR were used.

### 3.2.1 $^1$H-NMR

$^1$H-NMR experiments involve measuring the resonance frequencies of protons. As the resonant frequency is influenced by the environment of the proton it is possible to derive information about a molecule from its NMR spectrum. The underlying principles of NMR are grounded in quantum mechanics, below a brief description is given.

In quantum mechanics subatomic particles (electrons, neutrons and protons) can be imagined to be spinning on their own axis. Accordingly, the particles each have a spin angular momentum, $J$. In some nuclei the spins of neutrons and protons are paired against each so the nucleus has no net spin but in others the spins are not completely paired and the nucleus has a resulting net nuclear spin, $I$. The $^1$H nucleus, for example, contains a single proton which has a spin of $I = 1/2$ and as this spin is not paired the nucleus has a net nuclear spin of $I = 1/2$. In this case (and when $I \neq 0$ in general) the nucleus can be thought of as a spinning (positive) charge which from basic theory of electromagnetism is known to generate a magnetic field. This, in turn, gives rise to a magnetic moment, $\mu$, described by,

$$
\mu = \gamma J,
$$

(3.33)

where $\gamma$ is the gyromagnetic ratio, a fundamental nuclear constant that has a different value for every nucleus. In essence, the spin $I \neq 0$ nuclei are tiny bar magnets.
The quantum nature of the nucleus imposes certain restrictions on its behaviour. Most significantly, it only allows the nucleus to be in a fixed number of orientations which is related to its spin by \( 2I + 1 \). The reason for this is that the z-component of \( J \) is quantised and can, therefore, only take certain discrete values according to,

\[
\langle J_z \rangle = m \frac{\hbar}{2\pi}
\]

(3.34)

where \( m \) is the magnetic quantum number which can adopt values of \( m = -I, (-I + 1), ..., 0, ..., (I - 1), I \) and is used to describe each of the orientations. Ordinarily, the different orientations of the nucleus are of equal energy but when an external magnetic field is applied the energy levels of the orientations split giving rise to a population difference in the two levels according to the Boltzmann distribution. Fig. 3.4 illustrates the splitting of the energy levels for \( I = \frac{1}{2} \) nuclei such as \(^1\text{H} \).

![Figure 3.3 - Diagram of energy level splitting for spin \( \frac{1}{2} \) nucleus](image)
At a fixed temperature the Boltzmann distribution tells us that the lower energy level is more highly populated than the higher level. This means it is possible to promote some of the nuclei from the lower state into the higher state by exciting the system. Due to the quantised nature of the system, however, the excitation energy must be exactly equal to the difference in energy of the two levels which can be determined as follows. The energy of a single level is given by,

$$E = \mu_z B,$$

where $B$ is the magnitude of the magnetic field at the nucleus. By inserting Eqn. (3.33) into Eqn. (3.35) we have,

$$E = \gamma J_z B = \gamma m \frac{\hbar}{2\pi} B. \hspace{1cm} (3.36)$$

Therefore, the energy difference between the $m = -1/2$ and $m = 1/2$ states is,

$$\Delta E = \gamma \frac{\hbar}{2\pi} B. \hspace{1cm} (3.37)$$

The key point to realise in Eqn. (3.37) is that the excitation energy, $\Delta E$, is proportional to the magnetic field experienced at the nucleus and not the applied magnetic field. This means that $^1\text{H}$ nuclei experiencing different magnetic fields will be excited (or resonate) at different energies. So the next question is what might cause different nuclei in a given sample to experience different magnetic fields?

The answer to the above question is the electron. The $^1\text{H}$ atom has one proton in the nucleus which is orbited by a single electron. It has already been stated that the spin of the proton gives rise to a magnetic field. Similarly, the orbiting motion of the electron also generates a magnetic field. Unlike the
protons magnetic field, however, when an external magnetic field is applied the electron’s orbit is perturbed in a way that the magnetic field it generates opposes the external field. Consequently, the field experienced at the nucleus is slightly reduced, this effect is termed shielding. It follows that if the position of the electron’s orbit changes the electron generated field will also change resulting in a slightly different field at the nucleus. Thus, the variation in magnetic field (and thus resonant frequency) experienced by the nucleus is due to electron shielding. Finally, since $^1$H has a low electronegativity the position of the electron orbit about the $^1$H nucleus is strongly dependent on the atoms it is bonded to. Therefore, by measuring the different excitation (resonant) energies it is possible to reveal the chemical environment of a $^1$H from which details of the molecular structure of a molecule can be determined. Due to the chemical influence on the resonant frequencies of the nuclei the resonant frequency is often converted into an analogous parameter known as chemical shift.

In NMR experiments, a sample is excited by a burst of radio frequency (rf) energy containing a broad range of frequencies so that all the $^1$H nuclei in the sample are excited simultaneously. The energy emitted by the nuclei as they relax is measured. Since all the nuclei (with different resonant frequencies) are relaxing at the same time the measured signal is a superposition of all the frequencies of the $^1$H nuclei in the sample. The measured signal is, therefore, put through Fourier transform mathematical analysis software to convert the complex time-domain signal to the frequency domain. Additionally, the signal from numerous pulses are aggregated before analysis because the relaxation processes in the sample leads to an exponential decay of the emitted signal, which is referred to as the Free Induction Decay signal (FID).
3.2.2 Nuclear Overhauser Effect Spectroscopy (NOESY)

When two nuclei are in close proximity (< 5Å) the spins can undergo cross-relaxation. This cross-relaxation is a manifestation of the Nuclear Overhauser Effect (NOE). The NOE is observed as a change in intensity of one resonance when the intensity of the neighbouring resonance is perturbed. To better understand this, consider two $^1\text{H}$ nuclei with spin, $I$ and $S$, in very close proximity in a magnetic field aligned in the z-direction. From the above discussion it is known that these two nuclei would each have two possible orientations; one that is aligned with the magnetic field and thus of lower energy, $\alpha$, and another opposing the magnetic field and, therefore, of higher energy, $\beta$. Moreover, the nuclei will populate the two levels according to the Boltzmann distribution. If one was to then excite only one spin, $S$, for example, it would then return to the equilibrium state via some relaxation processes. The key is that the relaxation of $S$ can involve $I$ but only if the two nuclei are close enough to each other. This, in turn, can lead to a perturbation of $I$ which can be measured as a change in intensity of the $I$ resonance.

Fig. 3.5 illustrates the energy levels of the two-spin system and all the transitions between them. On the basis that NOE only occurs if the transition of one spin leads to a perturbation of the other spin it can be seen that there are only two possible transitions that gives rise to NOE build-up, these are $W_0$ and $W_2$. None of the other transitions involve cross-relaxation and thus do not contribute to NOE.
A NOESY experiment is essentially a series of $^1$H-NMR experiments, in which a particular frequency is selectively excited by way of a particular rf pulse sequence before measuring the emitted signal. The results are plotted on a 2D map and the NOE build-up appears as cross-peaks wherever intermolecular interactions occur. While quantitative analysis of NOE plots is difficult, the plots are extremely useful for determining the structures of large particles.

3.3 Dynamic Light Scattering (DLS)

DLS is a technique that enables the size of particles to be determined by measuring their mobility or diffusion in suspension. It has been widely used to study surfactant aggregation.\(^{80}\) The technique assumes that the particles move with Brownian motion, in which case two fundamental principles apply. Firstly, the probability distribution of particles is proportional to the translational diffusion coefficient, $D$, of the particles by\(^{61}\),

$$\rho(x,t) = \frac{1}{4\piDt^{\frac{3}{2}}} e^{-x^2/4Dt},$$

(3.38)
and secondly, the diffusion coefficient is inversely proportional to the hydrodynamic diameter of the particles, $D_H$, via the Stokes-Einstein relation,

$$D_H = \frac{kT}{3\pi\eta D}$$  \hspace{1cm} (3.39)

where $k$ is the Boltzmann constant, $T$ is the temperature and $\eta$ is the viscosity of the solution the particles are suspended in. Thus, by measuring the diffusion coefficient of particles it is possible to determine their size. It is important to note that Eqn. (3.39) is only true for spherical particles, meaning that the hydrodynamic diameter determined by this technique is actually the diameter of a sphere that diffuses with the same rate as the particle being measured. For non-spherical particles this means $D_H$ is only an estimate of the true particle size.

In order to determine the diffusion coefficient of a particle a DLS instrument first irradiates a sample with a laser light pulse and measures the rapid time fluctuations of the intensity of the scattered light. The fluctuations are analysed by an auto correlator which is essentially a signal comparator. It compares the intensity of light at time $t$ with the intensity at some initial time, $t = 0$ and determines the correlation between the signals. It is for this reason that DLS is sometimes referred to as photon correlation spectroscopy. For a randomly fluctuating signal it is obvious that there will be no correlation between the signal at $t = 0$ and $t = \infty$. However, after only a short interval, $\delta t$, one expects to see much greater correlation. As time elapses, therefore, the correlation between the initial and scattered signals will decrease and the rate at which the correlation decreases is related to the diffusion coefficient via the correlation function which is given by,

$$G(\tau) = \langle I(t)I(t+\tau) \rangle$$  \hspace{1cm} (3.40)
where \( \tau \) is the time delay between subsequent measurements of the scattered signal. For monodisperse particles \( G(\tau) \) is an exponentially decaying function of the time delay and can be expressed as,

\[
G(\tau) = A + B e^{-Dq^2\tau}
\]  

(3.41)

where \( A \) and \( B \) are constants of proportionality, \( D \) is the diffusion coefficient and \( q \) is the scattered wavevector and is given by

\[
q = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2}
\]  

(3.42)

where \( n \) is the refractive index of the sample, \( \lambda \) is the wavelength of the laser light and \( \theta \) is the scattering angle. It is worth noting that Eqn. (3.42) is the same as Eqn. (3.4) where \( q \) was introduced in the discussion of neutron scattering. To neutrons, however, the refractive index of air = 1, so \( n \) was not included in Eqn. (3.4). In this case the refractive index of the sample is > 1, so it must be included in the expression for \( q \).

For polydisperse samples, the correlation function is described by

\[
G(\tau) = A + B g_1(\tau)
\]  

(3.43)

where \( g_1(\tau) \) is the sum of all the exponential decays in the correlation function.

After measuring the correlation function software performs Cumulants analysis which is the process of fitting an exponential (or multiple exponentials in the case of polydisperse samples) to the correlation function. Finally, the calculated diffusion coefficient is converted to a hydrodynamic radius.

Another useful parameter determined by DLS is the polydispersity index (PDI). This is an estimate of the width of the size distribution obtained from the cumulants analysis.\(^{82}\)
3.4 Ultraviolet Spectroscopy (UV)

UV spectroscopy is most commonly used for the quantitative analysis of analytes. While the use of UV spectroscopy is becoming less common due to the increased availability of more powerful techniques such as NMR spectroscopy, UV spectroscopy still remains a useful experimental technique. A particularly attractive aspect of the technique is that UV spectrometers are significantly cheaper and smaller than other spectroscopic instruments. Additionally, use of UV spectroscopy requires less experience and expertise, meaning that it is a very convenient lab-based technique.

Another advantage of UV spectroscopy is that experiments are easy to perform. The procedure is as follows: first the absorption spectrum of a background is obtained - this is usually the spectrum of the solvent. Following this, the absorption spectrum of the sample solution is measured. Finally, the background is deducted from the sample spectrum to reveal the absorption from just the sample. In modern instruments the final step is automatically done by software so the user only sees the absorption spectrum of the sample.

While UV spectroscopy is a fairly simple experimental technique, the science behind the techniques is a little more complicated. There are three main mechanisms that lead to UV absorption. The primary mechanism is via excitation of an electron from the ground state to an excited state. The second mechanism is via changes in the vibrational state of a molecule. Finally, UV radiation can be absorbed by inducing changes in the rotational state of the molecule. Since each of these properties is governed by quantum mechanics it means that transitions from one state to another can only occur if the energy of a photon coincides exactly with the difference between two states. Accordingly, one might expect a UV absorption spectrum to consist of a number of sharp absorption lines with each line corresponding to a transition between electronic, vibrational or rotational states. In practice, however, this is not what
is observed and absorption spectra actually consist of numerous absorption bands. The reason for this is the high number of vibrational and rotational states that are available. While there are very few electronic transitions that can lead to UV absorption, there are numerous vibrational states for each electronic level and these are closely packed. For each vibrational state, in turn, there are a number of rotational states. Thus, photons with energy above and below the electronic transition energy can be easily absorbed, giving rise to continuous absorption bands.

Fortunately, quantitative analysis of absorption spectra is still fairly straightforward despite the complicated nature of UV absorption. In general, absorption follows the Beer-Lambert law which states that absorption is linearly proportional to the concentration of absorbing molecule and can be expressed mathematically as

\[ A_\lambda = \varepsilon_\lambda \cdot c \cdot l \]  \hspace{1cm} (3.44)

\[ c = \frac{A}{\varepsilon l} \]  \hspace{1cm} (3.45)

where \( \varepsilon \) is the wavelength-dependent absorption (or extinction) coefficient, \( c \) is the concentration of absorbing molecules and \( l \) is the path length through the sample. In a UV spectrometer, transmission, \( T_\lambda \), is a measured quantity and converted to \( A_\lambda \) using the following expression

\[ A = \log_{10} \left( \frac{100}{T} \right) = 2 - \log_{10} T \]  \hspace{1cm} (3.46)

Therefore, using Eqn. (3.44) it is possible to calculate the concentration of an absorbing molecule in any solution provided one knows its extinction coefficient at some wavelength. While in principle Eqn. (3.44) is true for all wavelengths it is preferable to evaluate the equation at the wavelength where
absorption reaches its maximum value for a given absorption peak, $\lambda_{\text{max}}$. The reason for this that this wavelength is likely to correspond to an electronic transition meaning that if there is a shift in the absorption peak between different samples one can still reliably compare the value of $A$ (at the new $\lambda_{\text{max}}$) since it still corresponds to absorption from the same mechanism. If one uses another wavelength it is not guaranteed that absorption from the same transition is being compared.

Values of $\varepsilon$ can be found in literature for many simple molecules but for more complex substances it must be calculated. This is done by measuring the absorption of samples of known concentration, then using the re-arranged form of Eqn. (3.44) ($\varepsilon = \frac{A}{cl}$) to calculate $\varepsilon$.

An important feature of UV spectroscopy is that the chemical environment of a molecule can influence its absorption spectrum. If, for example, a substance is dissolved in two different solvents with different polarities, it is common to see changes in both the shape of the absorption spectrum and more importantly the peak positions i.e. $\lambda_{\text{max}}$. This solvent effect was used by Riegelman et al. to predict the location of solubilisates in micelles. The absorption spectra of some solubilisates were determined in a variety of solvents with different polarities and then these spectra were compared to those of the solubilisate in the micelles. By finding spectra that shared the most features the chemical environment of the solubilisates in the micelles were determined. Since the core of a micelle is non-polar and the shell is polar it was finally possible to predict which part of the micelles the solubilisates were solubilised in.
3.4.1 Pesticide Partitioning

The octanol-water partition coefficients (LogP<sub>ow</sub>) provide reasonably accurate predictions for the location of solubilisates because the octanol-water mixture represents a fairly close approximation of the micellar environment available to a solubilisate. However, for alkyl ethoxylate micelles a more appropriate mixture is one composed of hydrocarbon and ethylene oxide as this corresponds directly with the core and shell of the micelle, respectively. In this work a mixture of dodecane and hexaethylene glycol was used to replicate the environment in the C<sub>12</sub>E<sub>6</sub> micelles.

As dodecane is insoluble in water, shell hydration was emulated by adding water to the mixture. Increasing volumes of water were used to study the effects of different amounts of shell hydration. The maximum amount of water added corresponded to approximately 2.5 molecules of water per ethylene oxide unit as neutron reflection experiments on C<sub>12</sub>E<sub>12</sub> at the air-water interface showed that each ethoxylate (EO) unit was associated to approximately 2 water molecules.\textsuperscript{75}
4 Effect of Surfactant Molecular Structure on Micellar Shape, Size and Nanostructure

4.1 Introduction

The main focus of this work was to try and develop a better understanding of the interactions and influences of some model pesticides on various non-ionic alkyl ethoxylate micelles. But in order to do this a good understanding of the pure micellar systems was required. Reviewing the literature on micelles revealed that the alkyl ethoxylate micelles had been generally well studied over the years, but there had been few systematic studies on the relationship between surfactant molecular structure and micellar structure. This was, therefore, outlined as a starting point for the study to characterise the influence of surfactant structure on micellar structure. In fact, knowledge of such a fundamental topic would not only be of benefit for the remainder of this study but is generally of great importance. It could not only aid the development of new products such as drug delivery systems\textsuperscript{84,85} and aqueous phase based agri-sprays\textsuperscript{7} in which micelles are employed as encapsulating agents, but also help improve existing products that rely heavily on surfactants such as cosmetics and detergents.

Theoretical studies have provided a fundamental understanding of the relationship between surfactant molecular structure and micellar structure (see Chapter 2) and in some cases quantitative predictions have also been made. But, in general, experimental data to support theoretical findings is lacking.
In this chapter we discuss the results of an experimental study in which the physical properties of micelles were measured with respect to the molecular structure of alkyl ethoxylate surfactants. SANS and DLS were used to determine the shapes and sizes of the micelles, $^1$H-NMR was used to investigate micellar hydration and NOESY NMR to reveal information about the internal structures of micelles. In total six surfactants were studied which belonged to two separate series, $C_mE_6$ and $C_{12}E_n$, in order to elucidate the respective influences of the head and tail groups.

4.2 Experimental

4.2.1 Materials

Five of the fully hydrogenated surfactants were purchased from Sigma-Aldrich, $C_mE_6$ (where $m = 10, 12 \text{ and } 14$) and $C_{12}E_n$ (where $n = 5$ and $8$), and were used without further purification. Fully hydrogenated $hC_{12}hE_{12}$ and chain deuterated $dC_{12}hE_{12}$ were provided by Dr RK Thomas at University of Oxford. $hC_{12}hE_{12}$ was prepared by reacting $hC_{12}hE_6$ with hexaethylene glycol (E6) (Fluka, > 98%), following the procedures described previously. $^{27}$ Dried $hC_{12}hE_6$ was first reacted with p-toluenesulphonyl chloride (Fluka, 99%) under dry triethylamine (Aldrich, 99%) to obtain $C_{12}E_6$-tosylate. In a separate flask, dried EO6 in excess was gently mixed with potassium tert-butoxide (Aldrich, 99%) to obtain K-EO6. When the reaction was complete, the sample was mixed with the $C_{12}E_6$-tosylate. The mixture was stirred and heated at $70^\circ C$ for 2h, followed by the addition of 10ml hot water to stop the reaction. When cooled, the mixture was neutralised with HCl and extracted with ether. Following solvent evaporation, the raw sample (light yellow oil) was purified through silica flash chromatography. Alkyl chain deuterated $dC_{12}hE_{12}$ was synthesised following a similar procedure as described above. $dC_{12}hE_6$ was made by the
Williamson reaction from the deuterated dodecyl bromide, an equimolar amount of sodium, and a 5-fold molar excess of E6.75

Surfactant solutions were prepared at 100 times their cmc by dissolving the required volume/mass of surfactant in 1 ml D2O (containing 99.9% D). The following cmc values were used: 0.90 mM for C_{10}E_6, 0.067 mM for C_{12}E_6, 0.010 mM for C_{14}E_6, 0.062 mM for C_{12}E_5, 0.10 mM for C_{12}E_8 and 0.10 mM for C_{12}E_{12}. For NMR experiments TSP (3-(Trimethylsilyl)propionic-2,2,3,3-d4 acid sodium salt) was added to the micellar solutions at a concentration of 1% w/v as a measurement standard.

### 4.2.2 Experimental methods

SANS experiments were conducted on the time-of-flight LOQ diffractometer at the ISIS neutron facility which has a q-range of 0.009 - 0.249Å⁻¹. Standard procedures for data treatment were employed. Measurements were performed in a 2mm quartz cell, using a 12mm diameter beam. The temperature for all experiments was kept constant at 295K to ensure samples remained in a single phase throughout the scattering experiment. After data collection completed the D_{2}O (solvent) scattering profiles were subtracted from beam intensities for background correction.

DLS was used to provide supporting information to SANS. DLS measurements were performed on a Malvern Instruments Zetasizer Nano instrument. Surfactant samples were loaded in quartz cells and left to equilibrate for 5-10 min prior to the measurements. For each sample, 3 measurements were taken consisting of 15 runs each. Each run lasted 5 seconds. Values for the hydrodynamic radius, \( R_H \), of the micelles were calculated by averaging 3 repeat measurements. The temperature for all measurements was kept constant at 295K.
NOESY spectra have been shown to be highly effective at investigating the internal structure of micelles\(^{88}\) while \(^1\)H-NMR can help reveal the extent of hydration of alkyl chain fragments within micelles.\(^{89}\) The \(^1\)H and NOESY spectra were recorded in D\(_2\)O on a Bruker Avance 400MHz spectrometer. Each spectrum consisted of 16 scans. The gradient NOESY spectra were recorded using a mixing time of 300 ms, and a relaxation delay of 2s and 2k data points were collected for 512 increments of 32 scans.

### 4.3 Head Length Effect

The influence of the surfactant head group was determined by studying the C\(_{12}\)E\(_n\) series of surfactants with \(n = 5, 6, 8\) and 12. For each surfactant the SANS scattering profile was obtained and fitted using the ellipsoidal core-chain model described in Sec. 3.1.3. The key details of the model are that the micelles have an ellipsoidal core with semi-axes \((a, a, c)\) and axial ratio \(e = a/c\) and a shell that is composed of head groups which behave like Gaussian chains with effective radii of gyration \(R_g\). The values of \(a, c\) and \(R_g\) for each micelle are determined by calculating the theoretical scattering cross-section using Eqn. 3.7 and fitting it to the experimental data by varying the three fit parameters.

In order to use Eqn. 3.7 correctly, a number of other values were also required including the scattering length densities of the core, head group and D\(_2\)O \((\rho_{\text{core}}, \rho_{\text{head}}\) and \(\rho_{\text{D}_2\text{O}}\)), the volumes of the surfactant head and tail groups \((V_H\) and \(V_C)\) and the aggregation number of the micelle, \(n_{\text{agg}}\). The scattering length densities were calculated using Eqn. 3.9. The volume of the core was calculated as \(V_{\text{core}} = 4/3 \pi a^2c\) while the volume of the tail, \(V_C\), was calculated using Tanford’s expression for the volume of a hydrocarbon chain given by Eqn. 2.6. The volumes of the head group\(^{90}\) and D\(_2\)O\(^{90}\) were taken as 61Å\(^3\) and 30Å\(^3\), respectively, and the aggregation number was calculated as \(n_{\text{agg}} = V_{\text{core}}/V_C\) since no holes can exist in the core and it is assumed that the core
is completely dehydrated. Using these values the experimental data was fitted. Figure 4.1 shows the experimental SANS scattering data and the fitted curves. The data sets have been arbitrarily translated in the vertical axis for clarity.

The first thing to notice in Figure 4.1 is that it was generally possible to fit the experimental data well with the ellipsoidal core-chain model, suggesting that all four surfactants form ellipsoidal micelles. Next, we see that there are significant changes in the shapes of the scattering profiles as \( n \) increases. This indicates that the micellar size and shape also change significantly as the head length increases. According to the relationship derived by Becher (Eqn. 2.3) the aggregation number of the micelles in the C_{12}E_{n} series should be inversely

\[ \text{Aggregation number} \propto \frac{1}{n} \]

\( n \) is the number of ethoxylate units in the head group. In this context, the head ‘length’ refers to the number of ethoxylate units in the head group as opposed to its actual physical length.
proportional to the head length. Analysis of the fit parameters reveals more information about the micellar aggregation numbers.

For \( \text{C}_{12}\text{E}_5 \), \( \text{C}_{12}\text{E}_8 \) and \( \text{C}_{12}\text{E}_{12} \), a single set of parameters gave a suitable fit to all the data points but for \( \text{C}_{12}\text{E}_6 \) two separate sets of parameters were necessary to achieve a good average fit. In Figure 4.1 the two sets of fitted parameters for \( \text{C}_{12}\text{E}_6 \) gave the blue dashed curves and the solid blue curve is the average of these curves. The necessity to fit two separate curves for \( \text{C}_{12}\text{E}_6 \) indicates that \( \text{C}_{12}\text{E}_6 \) micelles adopt more than one shape. Details of these shapes are discussed below. The single curves fitted for the other micelles, on the other hand, suggest that only a single micellar shape exists in these solutions. Table 4.1 lists all the fit parameters for the \( \text{C}_{12}\text{E}_n \) micelles. The dimensions of the semi-minor and semi-major axes of the micellar cores are represented by the values for \( a \) and \( c \), respectively. In order to ensure no void existed in the centre of the micelle one dimension was constrained to be smaller or equal to \( l_{\text{max}} \) (1.67nm) – the length of the fully extended alkyl chain calculated using Eqn. 2.4 – while the other dimension was freely fitted.

Table 4.1 shows that for \( \text{C}_{12}\text{E}_5 \), \( \text{C}_{12}\text{E}_8 \) and \( \text{C}_{12}\text{E}_{12} \) the shortest dimension is generally much smaller than \( l_{\text{max}} \). This is in fact consistent with Tanford’s theory\(^\text{13} \) which suggests that the shortest dimension of the micellar core will actually be close to \( 0.8 \times l'_{\text{max}} \) where \( l'_{\text{max}} \) is the length of the fully extended alkyl chain composed of \((n_c-1)\) methylene groups. The reason for this is that the \( \text{CH}_2 \) group closest to the ethoxylate head group protrudes into shell leaving \((n_c-1)\) \( \text{CH}_2 \) groups in the core. This chain then adopts a conformation such that its total length is shorter than its fully extended length. According to this description the maximum length of the shortest dimension of a micelle formed by surfactants with a \( \text{C}_{12} \) chain would be 1.22nm. The shortest fitted dimension for all the micelles is reasonably close to this value.
In the ellipsoidal model the shape of the micelle is determined by the axial ratio, $J = \frac{a}{c}$. When $J < 1$ the micelle is a prolate ellipsoid and when $J > 1$ the micelle is oblate ellipsoid. Thus, for $C_{12}E_5$ and $C_{12}E_6a$ the fittings indicate the formation of prolate micelles whereas for $C_{12}E_6b$, $C_{12}E_8$ and $C_{12}E_{12}$ oblate ellipsoids have been fitted to the data. Therefore, the data in Table 4.1 show that by increasing the length of head group by three EO units from $n = 5$ to 8 there is a shape transformation from prolate to oblate. Increasing the head length further does not cause any more changes in micellar shape but does lead to a slight reduction in the micellar core volume, $V_{\text{core}}$.

The observation of a shape transformation is interesting but the effect of the transformation on the shape of $C_{12}E_6$ micelles is even more striking. According to the two best fit curves and their corresponding parameters both prolate and oblate ellipsoids coexisted in the $C_{12}E_6$ solution. As the SANS scattering profile represents the average scattering from all species within a sample over the experimental time period (approx. 1hr) the data indicates that the two groups of micellar populations are in equilibrium. This is consistent with the findings of Baverback et al. which showed from SANS and SAXS that $C_{12}E_6$ micellar solutions consisted of multiple micellar shapes in coexistence.\[16\]

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**Table 4.1- Structural parameters obtained from the best fits shown in Figure 4.1 for $C_{12}E_n$ ($n = 5, 6, 8$ and $12$)**

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>SANS</th>
<th>DLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{12}E_5$</td>
<td>$a$ (±10%, nm)</td>
<td>$c$ (±10%, nm)</td>
</tr>
<tr>
<td>$C_{12}E_6a$</td>
<td>1.5</td>
<td>8.0</td>
</tr>
<tr>
<td>$C_{12}E_6b$</td>
<td>2.8</td>
<td>1.3</td>
</tr>
<tr>
<td>$C_{12}E_8$</td>
<td>2.3</td>
<td>1.3</td>
</tr>
<tr>
<td>$C_{12}E_{12}$</td>
<td>2.0</td>
<td>1.3</td>
</tr>
</tbody>
</table>

---
Glatter et al. also arrived at a similar conclusion using SANS but this time rather than directly fitting scattering profiles the conclusion was drawn after analysing the pair distance distribution function (PDDF) which was derived from SANS data. Some details of the shapes proposed in the three studies are given in Table 4.2.

Although all three sets of results agree that there are multiple micellar shapes in coexistence in C_{12}E_6 they do differ in the exact shapes attributed to the different micelles. This, however, is not of great importance since in SANS the specific shape attributed to a structure depends on the particular model used to fit the data. This means prolate, rod-like and cylindrical shapes can be viewed as essentially the same result. Likewise oblate (with low axial ratio), globular and spherical shapes are also practically the same. A more significant observation in Table 4.2 is that all three studies agree that the rod-like micelles are bigger than the oblate micelles. This observation is important because SANS is particularly sensitive to differences in size.

While none of the established theoretical models of micellisation predict the coexistence of micellar shapes an interesting observation is made when the packing parameter, $p$, is calculated for C_{12}E_6. Eqn. 2.9 showed that $p = V / a_0 l_c$, and using Eqns. 2.4 and 2.6 we find that $V_c$ and $l_c$ of the C_{12} chain are 323 Å$^3$ and 16.7 Å, respectively. The head group area, $a_0$, for C_{12}E_6 is found to

| Table 4.2 – Comparison of different data for C_{12}E_6 micelles |
|---------------------------------|--------------|
| Source                          | Method                        | Shape   | Relative Size |
| Current Data                    | SANS model fitting with contrast variation | Oblate  | Small         |
|                                 | SANS and SAXS model fitting    | Prolate | Large         |
| Baverback et al.$^{16}$         |                             | Sphere  | Small         |
|                                 |                             | Cylinder| Large         |
| Glatter et al.$^{45}$           | PDDF analysis from SANS      | Globular| Small         |
|                                 |                             | Rod-like| Large         |
be approximately \((55\text{ Å}^2)\) in literature. Putting these values into Eqn. 2.9 gives a packing parameter of \(p = 0.35\) which indicates that \(\text{C}_{12}\text{E}_6\) is very close to the transition boundary going from spherical micelles \((p < 1/3)\) to cylindrical micelles \((1/3 < p < 1/2)\). Thus, although the packing parameter theory does not explicitly mention the possibility of coexisting shapes the packing parameter of \(\text{C}_{12}\text{E}_6\) at the shape transformation boundary strongly suggests that some unusual behaviour should be expected. The experimental data indicates that this behaviour is the formation of multiple different shaped micelles.

This being said, it must also be remembered that one of the key assumptions made by Israelachvili et al. in the derivation of the packing parameter was that the head group area must be constant across the surface of the micelle which is not true for the ellipsoidal shapes proposed for \(\text{C}_{12}\text{E}_6\). Moreover, coexistence of multiple micellar shapes would also require some variation in the head group area between different micelles. In principle, therefore, the packing parameter does not support the observation of multiple micellar shapes. Indeed there are a number of other experimental studies which also suggest that only a single shape exists in \(\text{C}_{12}\text{E}_6\). Gapinski et al.\(^{35}\) and Penfold et al.\(^{37}\) claimed, for example, that \(\text{C}_{12}\text{E}_6\) formed rod-like micelles. However, even in these studies there is reason to believe the presented data could be consistent with the coexisting shape approach. For example, in the study by Gapinski et al. it was also indicated that the form factor for a tri-axial ellipsoid with dimensions similar to those for \(\text{C}_{12}\text{E}_6\) provided a close fit to their experimental data but the rod-like structure was arbitrarily chosen as an overall representative model.
Clearly then, there is some conflicting data with regards to the shape of C_{12}E_6 micelles. The classical view is that only a single shape of micelle exists whereas the more contemporary idea is that multiple micellar shapes coexist. Thus, we attempted to further support our own SANS analysis by varying the isotopic composition of the micelles and fitting the data.

Figure 4.2 shows the results of the H/ D contrast variation. The top set of data corresponds to hC_{12}hE_6 while the bottom set is for dC_{12}hE_6. The experimental data for both contrasts has been fitted using the same two sets of fit parameters as given in Table 4.1. In doing this, it can be seen that the average curves (solid lines) provide a reasonable fit to the experimental data under both isotopic compositions suggesting that the fitted parameters are reasonably accurate. If the fitted parameters did not represent the micellar shapes accurately then the simulated curves would generally only fit the data poorly.
experimental data for one particular composition. Therefore, the contrast variation method supports our conclusion that different micellar shapes coexist in the C_{12}E_{6} solution.

Coexisting populations have also been observed in cryo-TEM images of C_{12}E_{5} micelles. It was shown that small spherical micelles were in coexistence with long threadlike micelles. While our SANS fitting only revealed the long threadlike shape we attribute this to the fact that the radius of the spherical micelles is similar to the radius of the threadlike micelles and thus the smaller spherical micelles are hidden by the high scattering intensity at low-q from the large threadlike micelles.

The polydispersity index values, PDI, obtained from DLS measurements further support the observations made from SANS. It can be seen in Table 4.1 C_{12}E_{8} and C_{12}E_{12} both have small PDI numbers indicating that these micelles are rather monodisperse. For C_{12}E_{5} and C_{12}E_{6}, however, the PDI numbers are much larger, suggesting a higher degree of polydispersity which could be due to the presence of differently sized micelles, causing an apparent broad polydispersity.

Other interesting results revealed by the SANS data fitting are that there is only a small increase in $R_g$ with $n$, which suggests that in spite of the large transformation of core shape and size the conformation of the head group does not change significantly. The volume of the micellar core, $V_{core}$, on the other hand, which was calculated from the core dimensions for each micelle, varies significantly with $n$. It can be seen that the shape transformation is accompanied with an approximately ten-fold reduction in volume. Since the volume of the core is directly proportional to the average micellar aggregation number, $n_{agg}$, this translates to a ten-fold decrease in $n_{agg}$ too. The variation of $n_{agg}$ with $n$ is illustrated in Figure 4.3.
It can be seen that the relationship of $n_{\text{agg}}$ follows a hyperbolic path with $n$ consistent with the relationship derived by Becher in Eqn. 2.3. Becher, however, found that the aggregation number of $C_{12}E_8$ was 123 which is somewhat higher than the value obtained here 80. Since Becher’s value was obtained using basic light scattering measurements in the 1960’s, however, it is reasonable to suggest that our value of $n_{\text{agg}}$ is more accurate. Indeed in a more recent study using SANS by Zulauf et al. the aggregation number for $C_{12}E_8$ was found to be 95.38 This is still slightly higher than the value found from our data fitting but it is much closer than Becher’s value. One must, in fact, take caution when looking for micellar aggregation numbers in literature because many of the earlier studies give values far from what is being found with modern experimental techniques. The above values are one example of this, but an even more extreme example is in the $n_{\text{agg}}$ values obtained by Goto et al. using gas chromatography. It was suggested that the aggregation number of

![Figure 4.3](image.png)

**Figure 4.3** – Data points show the variation of $n_{\text{agg}}$ with surfactant head length, $n$. The solid curve is added as a guideline to highlight hyperbolic trend.
C₁₂E₆ micelles was around 250 – 350. Zulauf et al., on the other hand, found the aggregation number to be 140 which is in excellent agreement with our value of 141.

The $n_{agg}$ value for C₁₂E₁₂ 65 in Table 4.1 agrees less well with previously published values. For example, Penfold et al. reported a value of 79 for C₁₂E₁₂. As no obvious reason could be found for this discrepancy it was thought necessary to verify the model that was used to fit the data. This was done by two methods, firstly, by ensuring that the derived micellar shapes follow a consistent trend, i.e. a consistent shape transformation for the entire set of samples studied. Secondly, by fitting the derived micellar parameters for C₁₂E₁₂ to a second set of SANS profiles under different isotopic contrast. The former has already been shown in Table 4.1 and the contrast variation results are given below.

In Figure 4.4, the experimental SANS scattering profiles of fully protonated C₁₂E₁₂ (isotopic composition hC₁₂hE₁₂) and chain deuterated C₁₂E₁₂ (dC₁₂hE₁₂) are shown, with simulated curves of the best fit. As in Figure 4.2 the best fit curves were produced using the same ellipsoidal model and parameters as in Table 4.1 for both isotopic contrasts. It is clear that the simulated curves fit both sets of experimental data very well which verifies both the ellipsoidal model and the obtained parameters.

The two columns in Table 4.1 that have so far not been discussed are $R_{max}$ and $R_H$. $R_{max}$ represents the largest dimension of the micelle using values obtained from SANS fitting, i.e., it is equal to the sum of the largest dimension of a and c plus $2 \times R_g$. $R_H$ is the hydrodynamic diameter measured using DLS. These values are included to illustrate that $R_H$ is similar to $R_{max}$ for all C₁₂Eₙ micelles which is consistent with the physical implication of the hydrodynamic dimension.
Having seen such a significant change in the shape and size of micelles with $n$, it is expected to see an even greater change with tail length, $m$. This is because the tail length is responsible for micellisation as discussed in Sec. 2.3.1. The changes in scattering profiles as a result of increasing the alkyl chain length for fully protonated $C_mE_6$ ($m = 10, 12, \text{and } 14$) are shown in Figure 4.5. In this instance, the scattering profiles have not been translated in the vertical axis and the variation in absolute intensity arises from the different concentrations of the micelles.

It is seen that the shapes of the scattering profiles in Figure 4.5 resemble those seen in Figure 4.1, indicating that the micelles in the $C_mE_6$ series have similar shapes to those in the $C_{12}E_n$ series. The micellar parameters obtained from the data fit listed in Table 4.3 reinforce this observation. From the axial ratios of the micelles it can be seen that once again there is a shape
transformation. In this case, however, the transformation is opposite to that occurring when \( n \) is increased, i.e., there is an oblate-to-prolate transformation as \( m \) increases from \( m = 10 \) to 14.

Although this sort of shape transformation has not been previously reported for \( C_mE_n \) micelles, a similar transformation was observed by Arleth et al. in a mixed system of egg yolk phosphatidylcholine (PC) and polyethylene glycol (PEG) modified distearoyl phosphatidylethanolamine (DSPEPEG).\(^\text{92}\) In that system, DSPEPEG had a much bulkier head group and the mixed micelles were found to transform from oblate to prolate ellipsoid as the mole fraction of PC increased from 0 to 0.4. With respect to our system, increasing the PC mole fraction is analogous to increasing the chain length of the \( C_mE_n \) surfactant as PC lipid is effectively more hydrophobic than DSPEPEG. Thus, the preference

![Figure 4.5 - SANS intensity profiles for \( C_mE_6 \) (\( m = 10 \) (\( \downtriangle \)), 12 (\( \circ \)), 14 (\( \Delta \)) \) micelles. For \( C_{12}E_6 \) two best fitted curves are given because a good fit could not be achieved with a single set of parameters](image-url)
for prolate micelles when the hydrophobicity of the surfactant(s) is increased is consistent in both systems. Interestingly, the same form factor analysis was adopted in their work as has been here.

Accompanying the shape transformation we also see an almost ten-fold increase in the core volume. This is the same magnitude of volume change that was seen with the change in head group length but in that case the volume decreased. It may come as a surprise that the change in tail length caused the same volume change as head length changed because the thermodynamic theory of micellisation showed that the surfactant chain has a greater influence on the micelles. However, when one considers that in this case the tail length has only been increased by four methylene groups (\(-\text{CH}_2\text{-}\)\text{4} whereas the head group had been increased by seven EO groups (\(-\text{CH}_2\text{CH}_2\text{O}\text{-}\))\text{7} to achieve the same volume change one can see that the tail length does have a much bigger impact on the micellar size.

Table 4.3 shows that $R_g$ is constant with $m$, which suggests that there is practically no conformational change of the head group as the alkyl chain is increased.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>SANS $a$ (±10% nm)</th>
<th>SANS $c$ (±10% nm) $J$ (= a/c)</th>
<th>$V_{\text{core}}$ (nm$^3$)</th>
<th>$N_{\text{agg}}$</th>
<th>$R_g$ (nm)</th>
<th>$R_{\text{max}}$ (nm)</th>
<th>$R_H$ (nm)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{10}$E$_6$</td>
<td>2.3</td>
<td>1.0</td>
<td>2.30</td>
<td>21.2</td>
<td>80</td>
<td>0.55</td>
<td>3.4</td>
<td>3.4</td>
</tr>
<tr>
<td>C$_{12}$E$_6b$</td>
<td>2.8</td>
<td>1.3</td>
<td>2.15</td>
<td>46.5</td>
<td>141</td>
<td>0.55</td>
<td>3.9</td>
<td>5.3</td>
</tr>
<tr>
<td>C$_{12}$E$_6a$</td>
<td>1.5</td>
<td>8.0</td>
<td>0.19</td>
<td>75.4</td>
<td>233</td>
<td>0.55</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>C$_{14}$E$_6$</td>
<td>1.5</td>
<td>20.0</td>
<td>0.08</td>
<td>188.5</td>
<td>500</td>
<td>0.55</td>
<td>21.1</td>
<td>18.8</td>
</tr>
</tbody>
</table>

Table 4.3 – Structural micellar parameters obtained from the best fits shown in Figure 4.5 for C$_m$E$_6$ (m = 10, 12 and 14)
The trend in PDI values shown in Table 4.3 reflects that which was seen in the previous section. The small oblate C\textsubscript{10}E\textsubscript{6} micelles have low polydispersity while C\textsubscript{12}E\textsubscript{6} exhibits a much higher PDI value due to the coexistence of multiple micellar populations. C\textsubscript{14}E\textsubscript{6} also has a relatively high PDI value but it is not clear from this data whether this is due to coexistence of micellar populations (as with C\textsubscript{12}E\textsubscript{5}) or whether this is due to the dynamic nature of micelles which inherently leads to greater polydispersity in larger micelles. The R\textsubscript{H} values for all the C\textsubscript{n}E\textsubscript{6} surfactants are of the same order of magnitude as R\textsubscript{max} thus supporting the dimensions obtained from SANS modelling.

4.5 Hydrophile-Lipophile Balance (HLB)

The main conclusions drawn from the SANS data fitting are that increasing chain and head group lengths has opposite effects on the shape of the micelles and that C\textsubscript{12}E\textsubscript{6} consists of a distribution of micelle sizes. Moreover, the tail length has a much more significant influence on micellar size than the head. Our next step is, therefore, to attempt to characterise these changes using some convenient property of the surfactants. For this we chose the HLB due to its relevance in industry and in particular to the agrochemical industry. The extensive use of HLB for the formulation of emulsions has already been discussed. So it seems logical to also relate the properties of micelles to the HLB as this is an easy value to calculate and is already a familiar concept to people working in the field.

In Figure 4.6, the micellar core volumes from Table 4.1 and 4.3 for both series of surfactants are plotted against HLB which was calculated using Eqn. 2.1. The corresponding micellar shapes are also overlaid on the figure. The circles represent surfactants in the C\textsubscript{12}E\textsubscript{n} series and the diamonds denote the C\textsubscript{m}E\textsubscript{6} series.
The results shown in Figure 4.6 illustrate a rapid reduction in micellar volume as HLB increases when HLB < 12. The core volume reaches a plateau at around HLB = 13 and further increase in HLB has no effect on micellar shape. The trend is similar to what was observed by Diallo et al. for the C_{12}E_{m} series\textsuperscript{93} and is also very similar to that seen in Figure 4.3 which showed the change in micellar aggregation number with surfactant head length. The similarity in the trends shown in the two figures is in fact expected for the C_{12}E_{n} micelles since HLB is just a means of quantifying the surfactant head length and the core volume is another way of representing the aggregation number. In other words, Figures 4.3 and 4.6 essentially represent the same data for the C_{12}E_{n} micelles. The significance of Figure 4.6, however, is that it shows the same relationship between micellar size and chain length as that between

![Figure 4.6](image)

*Figure 4.6 – Changes in micellar core volume with HLB for the C_{12}E_{n} series (\textbullet) and the C_{m}E_{6} series (\textstar), with shape transitions also schematically represented. There is a sharp drop in micellar core volume around HLB = 12.5 where 2 different shapes of micelles coexist.*

*Note: micelle illustrations are not drawn to scale.*
micellar size and head length. This observation is not expected as it was also seen that only small changes in surfactant tail length were required to have the same effect on micellar size as seen from large changes in the head length. Clearly, when plotted in terms of HLB the difference in the influence of the head and tail on micellar size is lost and the relationship between micellar size and head and tail length is the same. This means that the size of a C\textsubscript{m}E\textsubscript{n} micelle can be predicted using surfactant HLB which is a very useful result.

In addition to the trend in micellar size, Figure 4.6 also illustrates the relationship between micellar shape and surfactant HLB. It is seen that for low HLB surfactants (i.e. hydrophobic surfactants) prolate or long rod-like shapes are preferred whereas for the more hydrophilic surfactants smaller more globular shapes are preferred. Thus, HLB numbers can also be used to predict the shapes of C\textsubscript{m}E\textsubscript{n} micelles. The ability to predict both size and shape using may have further implications on prediction of micellar solubilisation properties since the solubilisation capacity of a micelle is also related to its micellar size.

A final point to note about Figure 4.6 is that the HLB of C\textsubscript{12}E\textsubscript{6} is in the region where the change in micellar shape and size begins to reach the plateau. Therefore, one might argue that the existence of multiple micellar shapes and sizes is related to the rapid change in size with HLB. An alternative interpretation may just be that C\textsubscript{12}E\textsubscript{6} is a special case and the existence of multiple micellar shapes is due to its unique properties.

4.6 Shell Structure and Hydration

Having derived a relationship linking surfactant HLB with the shape and size of micelles we attempted to determine whether there are any changes in the internal structure of the micelles and the hydration of the shell associated with the shape and size transformation. This would enable us to understand more
clearly the relationship between surfactant molecular structure and micellar properties. This part of the study was performed using $^1$H-NMR and two-dimensional NOESY NMR.

4.6.1 $^1$H-NMR

The $^1$H-NMR spectrum for a C$_{12}$E$_6$ micellar solution at 100xcmc is shown in Figure 4.7a. Since the concentration of the surfactant is much greater than the cmc it is assumed that each of the peaks corresponds to micellar protons and the contribution from surfactant monomers is negligible. In this case, the chemical shifts of the peaks reflect the chemical environments of the proton species in the micelle.

In order to analyse the spectrum it was first necessary to identify which protons species each of the peaks correspond to. The peaks are identified as follows: 0.78ppm - terminal methyl group in alkyl chain, 1.2ppm - C$_9$H$_{18}$ bulk methylene alkyl chain, 1.45ppm - $\beta$-CH$_2$, 3.35ppm - $\alpha$-CH$_2$, 3.55ppm - ethoxylate head. It can be seen that there is a big separation between the $\alpha$-CH$_2$ and ethoxylate peaks the alkyl peaks. The reason for this is that the highly electronegative ether oxygens in the ethoxylate head de-shield nearby hydrogens causing them to experience a high chemical shift. By this same token, the terminal methyl protons are much more highly shielded causing them to appear at very low ppm.

On first glance, Figure 4.7a appears to be quite unremarkable. However, when the ethoxylate peak at $\delta \approx 3.55$ppm is viewed on an expanded scale as shown in Figure 4.7b an interesting observed is made. It is seen that the ethoxylate peak is in fact an envelope composed of a number of individual peaks. Moreover, the total number of peaks corresponds to the total number of EO units in the head. The integral values of the six peaks are shown in Figure 4.7b. It is seen that the integrals are of equal value indicating that the peaks
each represent the same number of protons. In other words, each peak must correspond to a single EO unit.

From NMR theory it is known that the magnitude of the chemical shift for any given proton is related to its chemical environment. Therefore, the

Figure 4.7 – (a) $^1$H-NMR spectrum of C$_{12}$E$_6$ and (b) ethoxylate peak on expanded scale is composed of a number of discrete peaks
separation of the EO peaks indicates that each EO unit experiences a unique chemical environment. This same behaviour was observed by Podo et al. in various non-ionic Triton X micelles. They attributed the effect to the ethoxylate units being associated with different numbers of water molecules.\(^\text{31}\) It was shown that the more hydrated an ethoxylate unit was the further downfield its peak was shifted. It was, therefore, claimed that the spreading of the ethoxylate peaks demonstrated the existence of a hydration gradient in the shell. Since the Triton X micelles have a similar structure to the \(\text{C}_n\text{E}_n\) micelles it is assumed that the spreading of the ethoxylate peaks in Figure 4.7b also occurs due to the existence of a hydration gradient in the shell of the \(\text{C}_{12}\text{E}_6\) micelles.

If a hydration gradient exists in \(\text{C}_{12}\text{E}_6\) then one would expect to find similar gradients in the other \(\text{C}_{12}\text{E}_n\) micelles. Indeed the NMR spectra confirm this. Figure 4.8 illustrates that the ethoxylate envelopes in all of the \(\text{C}_{12}\text{E}_n\) micelles is spread into a number of discrete peaks. The EO units closest and

![Figure 4.8](image)

*Figure 4.8 – Changes in shell hydration as demonstrated by changes in the chemical shift of ethoxylate protons. Dotted lines illustrate the boundary protons closest to and furthest away from the core*
furthest from the core have been labelled in the figure on the basis that increased hydration leads to a greater downfield shift (to higher ppm). It is seen that the chemical shifts of these units is almost constant for each of the micelles. This is because the EO unit furthest from the core is essentially in the bulk solvent and the EO closest to the core experiences the same hydrophobic properties from the core due to all the micelles having the same alkyl tail length.

An interesting observation in Figure 4.8 is that the number of discrete peaks for C\textsubscript{12}E\textsubscript{5} and C\textsubscript{12}E\textsubscript{6} corresponds to the number of ethoxylate units directly while for C\textsubscript{12}E\textsubscript{8} and C\textsubscript{12}E\textsubscript{12} some of the peaks at higher ppm begin to merge. This suggests that the hydration gradient is constant in the shorter head groups, but in the longer head groups the gradient must reduce further from the core. Moreover, the gradient for the shorter head groups must also be slightly steeper. If it is assumed that there is no water in the core and the maximum hydration of the ethoxylate units is 2.5 water molecules/ethoxylate unit then it is possible to approximate the hydration gradients in each of the micelles. Figure 4.9 illustrates the predicted gradients derived from the trend observed in Figure 4.8. It is important to note that Figure 4.9 plots the change in hydration against the EO unit number which is not the same as the distance from the core. Therefore, the spatial hydration gradients may vary somewhat, but the shapes of the gradients will be similar.
The observation of the hydration gradient has an important implication; it suggests that the core-shell model commonly used to fit SANS data for $C_{n}E_{n}$ micelles is inaccurate because it assumes homogenous hydration. This supports our use of the core-chain model to fit data since that model makes no assumptions about the hydration of the shell. Having said this, it is not clear what effect the hydration gradient actually has on SANS data. Given that the shell of $C_{n}E_{n}$ micelles is only around 0.6nm thick (see Table 4.1 and 4.3) SANS may not actually be sensitive to the hydration gradient. Nevertheless, the results show that a hydration gradient certainly exists and so the use of the core-chain model is justified despite the fact that it is slightly more complex than the core-shell model.

![Figure 4.9 – Prediction of hydration gradient in shells of $C_{12}E_{n}$ micelles](image-url)
4.6.2 NOESY

Having investigated the shape, size and hydration of the micelle the final area to be explored is the internal structure of the micelles. This study was achieved using NOESY NMR.

The underlying principle of NOESY is that pairs of protons in close spacial proximity (<5Å) give rise to a build-up of nuclear Overhauser effect (NOE). This NOE build-up can then be plotted as cross-peaks on a 2D map. Then, by identifying the chemical shift co-ordinates of the cross-peaks it is possible to reveal which protons are close together which, in turn, can help to derive the overall structure of a particle.

Figure 4.10a-c shows the NOESY plots for C₁₂E₆, C₁₂E₈ and C₁₄E₆ micelles. It is immediately clear that all three plots share the same general features; they each have a strong set of cross-peaks along the 45° diagonal (bottom left to top right) and two weaker sets of cross-peaks in the bottom right and top left. The diagonal peaks are characteristic of NOESY spectra and arise due to interactions of protons close to each other in a single molecule. For example, in a C₁₂E₆ surfactant the 3 protons on the terminal methyl group are very close to each other and thus give rise to NOE build-up. As the chemical shift of these protons is also the same the cross-peak appears along the diagonal. In a micelle, the cross-peaks of similarly positioned protons become even more intense because surfactants are generally closely packed and well aligned. Thus, in a micelle of aggregation number 50, for instance, there will be 150 hydrogen atoms from terminal methyl groups all in close proximity and all having the same ppm giving rise to a very intense cross-peak. Consequently, the diagonal cross-peaks can generally be ignored.
Figure 4.10 – 2D NOESY plots measured for aqueous solutions of (a) C_{12}E_{6} (b) C_{12}E_{8} and (c) C_{14}E_{6} micelles. All solutions were prepared at 100xcmc in D_{2}O.
The cross-peaks appearing away from the diagonal, however, are deserving of attention because these show interactions between protons in different chemical environments. In Figures 4.10a-c there are two such sets of cross-peaks off the diagonal; one in the bottom right and the other in the top left. In practice only one of these needs to be analysed because all the cross-peaks are mirrored in the 45° diagonal plane.

We chose to analyse the peaks in the bottom right of the spectra because these were slightly better resolved. Figure 4.11a-c shows the cross-peaks from the three full spectra on an expanded scale. It is found that the cross-peaks appear in two separate columns with chemical shifts of around 1.3ppm and 1.6ppm. From the 1H-NMR spectrum in Figure 4.7a it can be seen that these chemical shifts correspond to the bulk alkyl chain and β-CH₂ group, respectively. Thus, all of the cross-peaks in Figure 4.11a-c show interactions of the bulk alkyl chain and β-CH₂ protons. The protons these species are interacting with can be found from the chemical shifts of the vertical axis. The shifts are around 3.4ppm and 3.6 - 3.7ppm and, therefore, correspond to the α-CH₂ and ethoxylate head group, respectively. In other words, the cross-peaks shown in Figure 4.11a-c arise from interactions at the core-shell interface. Closer analysis of the peaks yields some interesting results.

In Figure 4.11a the cross-peaks have been separated into four main groups labelled 1-4. The origins of these groups are given in Table 4.4. Groups 1 and 3 represent interactions between β-CH₂ and α-CH₂ protons and α-CH₂ and bulk-alkyl chain protons. Given the dynamic nature of micelles and the constant exchange of surfactants with the bulk these interactions might be expected to occur. The interactions represented by groups 2 and 4, on the other hand, are not expected to occur since they indicate mixing of the hydrophobic tail and hydrophilic ethoxylate groups which is energetically unfavourable. Nevertheless, the presence of these peaks suggests that the head and tail
groups do intermix at the core-shell interface. Group 4 in particular suggests that the intermixing is quite extensive since it arises from the bulk alkyl chain being in close proximity to the ethoxylate head.

Intermixing of alkyl chains and ethoxylate head groups has been previously observed for a monolayer of non-ionic C_{12}E_{12} surfactants adsorbed at the air/water interface with neutron reflectivity\textsuperscript{75}, but this is the first time

Figure 4.11 – Cross-peaks from the bottom right region from Figure 4.10a-c corresponding to (a) C_{12}E_6, (b) C_{12}E_8 and (c) C_{14}E_6 micelles
Intermixing of the head and tails at the curved interface of micelles has been observed. Quantitatively we can infer that the cross-peaks correspond to the protrusion of the alkyl chain into the shell by exactly one CH$_2$ group (1 and 3) and more than two CH$_2$ groups (2 and 4). This is consistent with theoretical predictions from Tanford who suggested that the core of a micelle would be ‘rough’ and Aniansson who estimated from thermodynamic arguments that one CH$_2$ group protrudes into the shell from each monomer and one in seven monomers protrudes two or more CH$_2$ groups. A schematic of how this might occur in a micelle is illustrated in Figure 4.12. Sites of interaction that led to the observed cross-peaks are highlighted while surface roughness is represented by the dashed line.

The purpose of choosing C$_{12}$E$_6$, C$_{12}$E$_8$ and C$_{14}$E$_6$ for the NOESY study was to understand whether the difference in micellar shape and size influences the internal structure of the micelles. Since C$_{12}$E$_6$ was found to have coexisting globular and rod-like shapes, C$_{12}$E$_8$ micelles to form oblate ellipsoids and C$_{14}$E$_6$ long and prolate micelles these particular micelles were ideal for this purpose. It is clear from the observations made in Figure 4.11a-c that the same interactions occur in all three micelles and only vary in their magnitudes. This implies that the intermixing of head and tail groups at the core-shell interface of C$_m$E$_n$ micelles is essentially the same regardless of the shape or size of the micelles.

<table>
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<th>3</th>
<th>4</th>
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<td>β-CH$_2$</td>
<td>β-CH$_2$</td>
<td>bulk alkyl chain</td>
<td>bulk alkyl chain</td>
</tr>
<tr>
<td></td>
<td>α-CH$_2$</td>
<td>ethoxylate’s</td>
<td>α-CH$_2$</td>
<td>ethoxylate’s</td>
</tr>
</tbody>
</table>

Table 4.4- Interactions of hydrogens obtained from NOESY plots
4.7 Conclusions

Although SANS is most sensitive to the shortest and longest dimensions of a micelle, it is possible to approximate micellar shape by selecting an appropriate model for the form factor. Nowadays, a number of different models exist, so one must balance the complexity of the model (and thus amount of detail that can be extracted using it) with the amount of effort required to fit data. In the past, the core-shell model had been used in the study of alkyl ethoxylate non-ionic surfactant micelles due to its simplicity, but discrepancies with findings obtained from other experimental techniques suggested that this model did not accurately describe these micelles. Accordingly, we used an alternative model. On the whole, the results obtained from this model are consistent with previous results, however, a couple of key differences have been observed. Firstly, for C_{12}E_6, previous studies have generally attributed either prolate or

Figure 4.12 - Cartoon schematic of the core-shell interface of a spherical micelle. The highlighted regions illustrate the sites of interaction that led to the cross-peaks in the 2D NOESY plot in Figure 4.11c. The dashed curve demonstrates the ‘surface roughness’ of the core-shell interface.
oblate shapes to this micellar system but our analysis has led us to believe that multiple populations of different micellar shapes coexist. This has in fact been reported before but it is the first time it has been verified using a contrast variation approach with SANS. Moreover, the result is consistent with the general features observed for C$_{12}$E$_5$ micelles from cryo-TEM imaging. The second observation was that the aggregation number for C$_{12}$E$_{12}$ that we obtained was somewhat lower than that obtained using the standard core-shell model. This is possibly due to the greater influence of inhomogeneous hydration on SANS scattering for the longer head group surfactant.

In addition, a clear micellar shape transformation was observed with surfactant molecular structure. This shape transformation is accompanied by a change in micellar core volume. To present the data clearly, the shape transformation and volume change with changes in the surfactant head and tail group lengths were plotted against HLB (Figure 4.6) – an arbitrarily defined but extensively used variable in industry. The rapid reduction in core volume that occurs when HLB is increased from 11 to 13 is accompanied by a sharp shape transition from prolate to oblate ellipsoid and surfactants whose HLB falls within this range (e.g. C$_{12}$E$_6$) have two forms of stable micelles in coexistence. The actual scenario could be that many different micellar size distributions coexist within the range that were represented by the two geometries modelled.

In reality, the attributed shapes must be treated with caution as they depend entirely on one’s interpretation of data. For example, there is no geometric difference between a short prolate ellipsoid (rod-like) and an oblate ellipsoid (disk-like) from the perspective of data modelling. This being said, if one is able to derive a consistent trend/shape transformation, as has been achieved here, the data can be viewed with much more confidence. The fitting of chain deuterated non-ionic dC$_{12}$hE$_{12}$ and fully hydrogenated hC$_{12}$hE$_{12}$ in
D$_2$O to the same structural model added further credibility to the data interpretation.

Transition in size and shape in the surfactant series did not appear to affect the structural conformation of the ethoxylate heads as reflected from the almost constant radius of gyration. In parallel, some interesting hydration behaviour within the hydrophilic shell was observed. There was a clear hydration gradient extending from the core to the outer ethoxylate units, with the most dehydrated ethoxylate unit being the one closest to the core and the most hydrated unit being the one on the outer shell surface.

The 2D NOESY experimental data illustrated intermixing or ‘surface roughness’ within the micellar core-shell interface, represented by alkyl chain staggering and protrusion into the shell region. The NMR results further emphasised the inadequacy of the standard core-shell model in the study of non-ionic alkyl ethoxylate surfactant micelles.
5 Influence of Pesticides on Micellar Structure

5.1 Introduction

Having found a relationship between the molecular structure of C\textsubscript{m}E\textsubscript{n} surfactants and their micellar structure the next aim is to identify the influence of solubilisation on the structural characteristics of the micelles. To study this, two model pesticides, Cyprodinil (CP, 4-cyclopropyl-6-methyl-N-phenylpyrimidin-2-amine) and Diuron (DN, 3-(3,4-dichlorophenyl)-1,1-dimethylurea) were chosen as the probe solubilisates. The two series of surfactants that were studied in the previous chapter, C\textsubscript{12}E\textsubscript{n} and C\textsubscript{m}E\textsubscript{6}, were used again here.

The molecular structures of the two pesticides are given in Figure 5.1. As far as pesticides go, these are relatively simple molecules but represent the key general features of typical pesticide molecules. In terms of solubilisation studies the structures are quite complex. Previous studies in this field have tended to focus on the solubilisation of alkanes, simple alcohols, small aromatics and dyes which are generally more basic structures than these pesticides. Indeed there have been some studies on the solubilisation of more complex substances such as pharmaceutical drugs\textsuperscript{95,96} and perfumes\textsuperscript{40,64,97} but few generalisations about their influence on the structural characteristics of micelles have been drawn. Accordingly, it is extremely difficult to predict the behaviour of the pesticides in micellar solution from existing knowledge.

CP contains two aromatic compounds, a benzene ring and a pyrimidine and although the behaviour of benzene in micelles is fairly well understood,
the behaviour of pyrimidine is not. Moreover, the presence of the nitrogen linking the two rings will also affect its behaviour through the influence of H-bonding. In comparison, DN only contains a single benzene ring but it also has N, O and Cl atoms making its behaviour more difficult to predict.

A combination of UV and NOESY NMR was used to determine the amount of solubilisation and location of the pesticides. NOESY NMR was also used to study the internal structure of the micelles. The shape and size of the micelles was measured using SANS.

5.2 Experimental

5.2.1 Materials & Methods

Cyprodinil and Diuron (provided by Syngenta AG) were used without further purification. Solubilised micellar solutions were prepared as follows. First adding excess amounts of pesticide to 1ml vials of D₂O (containing 99.9% D) and sonicating for 5 minutes. This aided the solubilisation processes by dispersing the pesticide granules to small particle sizes. Then surfactant was dissolved in the pesticide solution to make the total surfactant concentration
equal to 100 times their cmc. For cmc values of the surfactants see Sec. 4.2.1. The micelle-pesticide solutions were then allowed to equilibrate at constant temperature (295K) for 5 days on a rocking plate. The solubilised solutions were centrifuged at 6500 rpm for 5 minutes and the supernatants were then extracted for measurements.

For NMR experiments d-TSP (3-(Trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt was added to the micellar solutions at a concentration of 1%w/v as a measurement standard.

SANS, ¹H and NOESY NMR experiments were conducted as detailed in Sec. 4.2.1.

Pesticide partitioning experiments were performed as follows. (1) The UV spectrum of a known amount of pesticide in 0.5ml dodecane was obtained. (2) Following this, 0.5ml hexaethylene glycol was added to the hydrocarbon and allowed to equilibrate for 5 minutes. (3) After the equilibration the UV spectrum of the dodecane partition was measured again. (4) The dodecane was then returned to the hydrocarbon-ethoxylate mixture. (5) The required volume of water was added to the mixture and the mixture was shaken. (6) Following this the mixture was again allowed to equilibrate for 5 minutes before measuring the UV spectrum of the dodecane. Steps 5 and 6 were repeated to give hydration amounts of 1H₂O/EO₆ molecule, 1, 1.5, 2 and 2.5H₂O/EO unit. The quantity of pesticide in the hydrocarbon partition was calculated using Eqn. (3.45).

5.3 Solubilisation Capacity

The first thing we set out to measure was the amount of pesticide solubilised in the micelles as this might give an indication of how strongly the pesticides influence the micelles. The solubilisation capacities of the micelles were found using integral values from ¹H-NMR spectra as follows. First the peaks in the
$^1$H-NMR spectra of a solubilised micelle system were identified as shown in Figure 5.2. Then the integral value of one of the pesticide peak integrals was calibrated to be equal to the total number of protons represented by that peak. Next, the value of this integral was compared to one of the surfactant peak integrals to find the ratio of surfactant molecules to pesticide molecules. Finally, the concentration of pesticide was calculated from the known concentration of surfactant.

As a worked example of the above method consider the following. In Figure 5.2 the H1 peak is calibrated to have a value of 2 since it corresponds to two aromatic protons (see inset). Doing this gives an integral value of 9.6 for the $\beta$-CH$_2$ (at 1.5ppm). Since the two H1 protons correspond to a single pesticide molecule and the two $\beta$-CH$_2$ protons correspond to a single surfactant the integral value for the surfactant must be divided by 2. This results in a ratio of 1:4.8 pesticide molecules to surfactants. Finally, this ratio is
converted to a molar solubilisation ratio (MSR) i.e. number of mole pesticide per mole of surfactant. Table 5.1 gives the MSR values for CP and DN in each of the micelles studied.

The general trend observed in Table 5.1 is that increasing the head and tail lengths of the $C_mE_n$ surfactants leads to an increase in MSR for both pesticides. The increase in MSR with tail length can be justified on the basis that the pesticides are solubilised in the core and since increasing the tail length effectively provides ‘more core’ to solubilise the pesticides in it is logical to see an increase in MSR. The same justification clearly cannot be used to

<table>
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<th>Surfactant</th>
<th>MSR</th>
<th>Pesticide:surfactant weight ratio (mg/mg)</th>
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<tr>
<td><strong>CP</strong></td>
<td></td>
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<tr>
<td>$C_{12}E_5$</td>
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<td>N/A</td>
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<tr>
<td><strong>DN</strong></td>
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</tr>
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</table>
describe the increase in MSR with head length since in this instance the hydrocarbon chain length remains constant. However, as was seen in Chapter 4 increasing the head length does lead to a reduction in micellar size which increases the solubilisation efficiency of the micelles.

The second column in Table 5.1 gives the MSR in terms of the weight ratio. This information is more valuable in industry because surfactants are purchased by weight. Therefore, it is more cost effective to use a surfactant with a high weight solubilisation ratio (WSR) than MSR. It is seen that when viewed in terms of WSR there is a reverse in the trend observed for MSR and increasing the head length leads to a reduction in WSR. The reason for this reversal is that the ethoxylate units have a relatively high molar mass. Therefore, increasing the head length by only one or two EO units leads a large change in its mass which translates to a lower WSR. For the tail length the trend is preserved and increasing the tail length also leads to an increase in WSR.

5.4 Cloud Point

It is seen that there is no MSR value for the C_{12}E_{5} + CP system in Table 5.1. The reason for this is that the C_{12}E_{5} micellar solution turned cloudy after addition of CP indicating that the solution had undergone a phase transition. The cloudy appearance resembled the appearance of a pure micellar system when the temperature is raised above the cloud point. Mitchell et al. showed that in the case of pure micelles the cloudy appearance is due to the coexistence of two separate phases in solution; a water phase in which the free surfactant concentration is fixed at or just below cmc and a micellar phase which has a low water content but high micelle concentration. Therefore, the cloudy appearance of the C_{12}E_{5} + CP solution indicated that the cloud point of the surfactant had been reduced. To verify this, the solution temperature was reduced and as expected the solution became clear. The significance of this
observation is that the reduction in cloud point implies that the micellar shell had been dehydrated.

To explore this idea further, the cloud point and temperature dependence of the size of pure and CP solubilised C$_{12}$E$_6$ micelles was studied using DLS. If CP was actually causing the micellar shell to dehydrate then one would expect not only a reduction in cloud point but also a more pronounced temperature effect. Figure 5.3 shows the difference in the temperature dependence of micellar size for the solubilised and un-solubilised micelles. The first observation is that the cloud point of the pure C$_{12}$E$_6$ micelles is around 47°C which is in excellent agreement with the 45°C reported by Mitchell et al. Next we can see that the cloud point of the solubilised micelle is indeed lower than the pure micelles. In fact, the cloud point of the C$_{12}$E$_6$ + CP micelles was found to be between 31 and 32.5°C, approximately 15°C lower than that of the pure micelles. This is quite a significant reduction implying quite extensive

![Figure 5.3](image_url)

**Figure 5.3** - Temperature dependence of hydrodynamic radius of C$_{12}$E$_6$ micelle with (pink, □) and without (blue, ●) CP. Presence of CP clearly causes micelles to grow much more quickly
dehydration. This is reflected in the temperature dependence as well. The hydrodynamic radius of the pure micelles increases almost linearly with temperature until reaching the cloud point whereas the size of the CP solubilised micelles only increases linearly at low temperatures then at around 27°C the radius begins to increase much more rapidly. Moreover, even in the linear region the rate of micellar growth is higher for the solubilised micelles. Therefore, the data presented in Figure 5.3 strongly supports the theory that solubilisation of CP causes the micellar shell to dehydrate.

Interestingly, solubilisation of DN did not cause cloudiness in the C_{12}E_{5} solution which implies the cloud point does not drop significantly with this pesticide. While this could indicate that DN does not cause dehydration of the micelle a more likely reason for is that the amount of DN solubilised in the micelle much lower meaning that the extent of dehydration is less.

5.5 Shell Hydration

The idea that the solubilisation of pesticides causes dehydration of the micellar shell is very interesting and was, therefore, investigated further using ^1^H-NMR. Figure 5.4 and 5.5 show the EO peaks before and after CP and DN solubilisation, respectively. The pesticides clearly cause the head group peaks to shift upfield and in the case of CP the peak envelopes are also considerably broadened. The greater influence of CP on the peak positions is attributed to the fact that its MSR is generally higher than DN.

Given that the splitting of the EO peaks is due to the presence of a hydration gradient both of the characteristic effects highlighted by Figure 5.4 and 5.5 indicate that the pesticides are indeed influencing the hydration of the shell. As the shift in the peaks is upfield (towards lower ppm) this suggests that there is a net reduction in the hydration. The broadening of the envelope indicates that the hydration gradient becomes steeper. Thus, the ^1^H-NMR
spectra confirm that the pesticides cause shell dehydration is predicted from the change in cloud point.

Figure 5.4 – ¹H-NMR spectra of EO head groups before solubilisation shows the existence of hydration gradients in the micelle shell. Spectra of EO head groups after CP solubilisation shows that the presence of pesticide affects the hydration gradient.

Figure 5.5 – ¹H-NMR spectra of EO head groups before and after DN solubilisation reflect findings from CP solubilisation.
Further verification was found by comparing the influence of the pesticides on the EO peaks to that of \( \text{NaH}_2\text{PO}_4 \) salt. Salts in general are known to dehydrate the micellar shell but \( \text{NaH}_2\text{PO}_4 \) is believed to be a particularly good dehydrating agent\(^{98}\). Thus, if the influence of this salt was the same as the pesticides this would strongly support the dehydration theory.

Figure 5.6 shows the EO peaks of \( \text{C}_{12}\text{E}_6 \) without any additional components (bottom), with \( \text{NaH}_2\text{PO}_4 \) salt (second bottom), with DN (second from top) and with CP (top). The dashed line is aligned to the final large peak of the pure \( \text{C}_{12}\text{E}_6 \) micelle. It can be clearly seen that the head group envelope is upfield shifted for the micellar solution with salt confirming that the upfield shift is indeed associated with shell dehydration.

### 5.6 Pesticide Location

In the next part of the study we attempted to determine the location of the pesticide molecules in the micelle because this was outlined as a key factor in determining the influence of solubilisates in micelles. We investigated
pesticide location by a combination of a simple partitioning experiment and NOESY NMR.

5.6.1 Hydrocarbon-Ethylene Glycol Partitioning

Measuring the partitioning behaviour of a substance between two solvents is a common technique in industry as it indicates which environment the substance would prefer to be in. One of the most common partitioning mixtures is octanol and water. In this mixture, octanol is non-polar and thus represents an oil-like phase whereas water is used to represent polar solvents. Substances are added to the mixture and allowed to partition between the two. The quantity in each partition is measured and the final ratio is presented as the logarithm of the ratio, the LogP<sub>ow</sub>. Substances with a high LogP<sub>ow</sub> have a preference for the octanol partition and are thus said to be hydrophobic while low LogP<sub>ow</sub> values indicate hydrophilic substances. The use of this particular mixture is common because it provides a measure of the overall hydrophobicity of a substance. For CP and DN the LogP<sub>ow</sub> values are 4.0 and 2.9, respectively, indicating that both substances are quite hydrophobic but CP is the more hydrophobic of the two substances.

According to the standard theory of solubilisation the location of a solubilisate in a micelle depends on its LogP<sub>ow</sub> value. Thus, the theory would suggest that CP would be solubilised in the core while DN would prefer to be in or near the palisade layer. There is, however, a flaw in this theory as explained below.

The LogP<sub>ow</sub> indicates which environment a substance prefers; polar or non-polar. In a C<sub>m</sub>E<sub>n</sub> micelle the polarity of the different domains is less well defined. Indeed the core and shell are non-polar and polar, respectively, but the shell is not particularly well represented by a water phase. For example, it would not be unusual for a substance to be insoluble in water but soluble in
the ethoxylate shell despite the hydrophilic nature of ethoxylate. Accordingly, the octanol-water mixture is not a good mixture for predicting the partitioning of substances in alkyl ethoxylate micelles. A much more suitable mixture is one of an alkane and a poly(ethylene glycol)(PEG, -OHCH\textsubscript{2}CH\textsubscript{2}OH-). In this mixture the substance would be presented with almost the exact environments that would be present in a C\textsubscript{m}E\textsubscript{n} micelle, meaning that its behaviour in this mixture would be much more indicative of its behaviour in an octanol-water mixture.

One might argue that even the PEG-alkane mixture is not an entirely accurate representation of the micellar environments because the PEG molecules have an extra hydroxyl group per molecule compared to the ethoxylate head groups in the micelle and, moreover, the PEG molecules have more freedom than the ethoxylate head groups which are anchored at the core-shell interface in micelles. But in reality these inaccuracies are not likely to be of any major consequence since the bulk environments in the mixture will be very much like those present in the micelle. In any case the PEG-alkane system is certainly more suitable than the octanol-water mixture and since the latter mixture has given reasonable agreement to experimental data it is reasonable to expect the PEG-alkane system to give even better agreement.

In order to perform the partitioning experiment it was essential that the two solvents were immiscible as mixing of the solvents would not allow for pesticide to partition correctly. The two solvents that were, therefore, chosen were dodecane and hexaethylene glycol. Dodecane is a relatively long chain alkane and is thus extremely hydrophobic, meaning that it does not mix with the much more polar hexaethylene glycol. These two solvents also coincide with the structure of C\textsubscript{12}E\textsubscript{6}. 
To make the partitioning mixture even more closely resemble the micellar environments, water was added to the mixture. Water is immiscible in the hydrocarbon partition, so it was assumed that all the water hydrated the PEG phase. Since a hydration gradient exists in the micellar shell (see Chapter 4) the effects of different amounts of shell hydration were also studied by varying the amount of water added to the mixture. The maximum amount of water added to the mixture equated to 2.5 H$_2$O molecules per ethylene glycol unit as this is believed to be the average hydration in the micellar shell.

In order to use Eqn. (3.43) to calculate the concentrations of pesticides in the dodecane partition from UV spectra the extinction coefficients of the pesticides in dodecane were required. For DN a value of 20000 ml mg$^{-1}$ cm$^{-1}$ at 250nm was obtained from literature$^{99}$ while for CP the extinction coefficient was calculated by measuring the absorption spectrum for a known concentration and then using Eqn. (3.43). Using this method a value of 23265 ml mg$^{-1}$ cm$^{-1}$ at 270nm was obtained. The difference in absorption spectra of the two pesticides in dodecane is illustrated in Figure 5.7. It can be seen that both pesticides have an absorption peak at around 215nm, attributed to the

![Figure 5.7 - UV absorption spectra of CP (pink) and DN (blue)](image)

Figure 5.7 - UV absorption spectra of CP (pink) and DN (blue)
benzene ring. The peak wavelength of the second peak is different. The second peak was used for calculations in both cases. The difference in absolute magnitude of the spectra is due to a difference in concentration.

The results of the partitioning experiment are illustrated in Figure 5.8. It can be seen that both pesticides exhibit similar partitioning behaviour. Initially, when no water has been added to the mixture a majority of the pesticide resides in the hydrocarbon partition (70-90%). But when water is added to the PEG phase the pesticides move out of the hydrocarbon and into the PEG. Only about 20-40% of the pesticides remain in the hydrocarbon partition. This behaviour is completely counter-intuitive since both pesticides are thought to be hydrophobic (according to their LogP_{ow} values). In contrast to what is actually observed one would expect to see more pesticide move to the hydrocarbon partition as water is added to the PEG in order to avoid interactions with water molecules. In essence, what Figure 5.8 suggests is that
the hydrated PEG partition is actually a better solvent for the pesticides than pure hydrocarbon and water.

With respect to their behaviour in micelles the results of the partition experiment indicate that only about 25% of the pesticides will be in the hydrocarbon core while the remainder will be solubilised in the shell. This contradicts the standard theory of solubilisation which predicts that both pesticides would solubilise in the core due to their high LogP_{ow} values. Verification of the result is hence required through NOESY measurements for more direct evidence.

5.6.2 NOESY NMR

In Chapter 4 NOESY NMR was used to study the internal structure of pure surfactant micelles. This was done by analysing the chemical shift co-ordinates of cross-peaks in NOESY plots. Using the same approach it is possible to determine the locations of a solubilisate in a micelle. One simply needs to identify which proton species in the solubilisate and micelle are in close proximity and the location of the solubilisate can be found. While the method is quite simple in principle there are a couple of caveats. Firstly, the concentrations of solubilisate and surfactant in the monomeric form in the bulk must be low so that their contribution to cross-peak formation is small. Secondly, the concentration of solubilisate in the micelle must be relatively high in order for it to provide a measurable NOE build-up. In the two micelle-pesticide systems studied here, the former was easily satisfied since the solubility's of CP and DN in water are extremely low at 12\(\mu\)g/ml and 35\(\mu\)g/ml, respectively. Additionally, the \textit{cmc} values of the surfactants studied are also quite low (typically 20-30\(\mu\)g/ml, with the exception of C_{10}E_{6}), such that interactions between the surfactants and pesticides in the bulk solvent will be negligible. However, the latter caveat was not satisfied for DN because its
solubility in all of the micelles was extremely low. Therefore, it was not possible to obtain reliable NOESY data for DN solubilised systems and only the location of CP was analysed using NOESY.

The NOESY plot for the C<sub>12</sub>E<sub>6</sub> + CP solution is given in Figure 5.9. The characteristic strong cross-peaks along the 45° diagonal are once again observed. But there are also many cross-peaks appearing away from the diagonal. As mentioned in the previous chapter the cross-peaks appearing away from the diagonal illustrate interactions between chemically different protons and are thus worthy of analysis. But in order to do so, it is first necessary to identify the chemical shifts of all the proton species in the sample. The chemical shifts for the micellar protons were the same as those identified in the previous chapter; 0.78ppm – terminal methyl group in alkyl chain -CH<sub>3</sub>, 1.20ppm – bulk methylene alkyl chain -C<sub>9</sub>H<sub>18</sub>, 1.45ppm – β-CH<sub>2</sub>, 3.35ppm – α-

![Figure 5.9 - 2D NOESY plot measured for aqueous C<sub>12</sub>E<sub>6</sub> micelle solution with Cyprodinil. Two sets of cross-peaks are circled. Dashed circle shows interactions between pesticide and core protons while solid circle shows interactions between terminal methyl protons and ethoxylate protons.](image-url)

CH$_2$, 3.55ppm - ethoxylate head -(OCH$_2$CH$_2$)$_6$. In addition to these peaks there are a number of other peaks corresponding to the CP protons. These were more clearly illustrated in Figure 5.2 - the $^1$H-NMR spectrum of the C$_{12}$E$_6$ + CP solution.

In Figure 5.2 there is one large peak at around 4.85ppm, this is the residual HDO peak which is characteristic of all NMR experiments performed in D$_2$O and can, therefore, be ignored. The four smaller peaks much further downfield at around 6 - 8ppm correspond to the benzene protons in CP as illustrated by the labels H1-4. The peak at around 2.4ppm labelled H5 is attributed to the CP methyl group and finally, the two very small peaks, labelled H6 and H7, correspond to the isopropane protons. It will be seen later that the particular positioning of these peaks between the surfactant bulk alkyl chain peak and the surfactant methyl peak is very important. The corresponding peaks in the NOESY spectrum in Figure 5.9 are also shown.

Having determined the chemical shifts of the pesticide proton species it is possible to proceed and analyse the cross-peaks. There are two sets of cross-peaks away from the diagonal. The first group to be considered is that found in the top left corner of Figure 5.9. The co-ordinates of these cross-peaks are approximately 6.47-1.2ppm, 6.80-1.20ppm, 7.14-1.20ppm and 7.67-1.20ppm which correspond to the aromatic protons in CP and the alkyl methylene protons. This particular group of cross-peaks might suggest that the pesticide is solubilised in the core. However, one must also bear in mind that the chemical shifts of the isopropane protons are also close to the bulk methylene chain protons as seen in Figure 5.2. Thus, it may be that this group of cross-peaks simply show that the aromatic protons are close to the isopropane protons. To determine whether this is the case the cross peaks are shown on an expanded scale in Figure 5.10.
In the expanded scale, it is seen that the four aromatic species have cross-peaks at the same chemical shift on the F1 axis. However, H1 and H4 both have additional cross-peaks at slightly lower chemical shift on the F1 axis. It is these extra cross-peaks at lower chemical shift values that correspond to interactions of the aromatic protons with the isopropane protons. Therefore, the four main peaks do in fact show that aromatic species H1-4 are all in close proximity to the bulk methylene chain. This verifies that the pesticide is close to the core of the micelle.

The above result is consistent with the standard theory of solubilisation which predicts from the high LogP_{ow} value of CP that it would be solubilised in the core. However, the result also seemingly contradicts the findings from the partitioning experiment presented above which indicated that the pesticide would be solubilised in the hydrated ethoxylate region. While this is initially quite puzzling, it is important to remember that NOESY is a direct measurement of the pesticide location whereas the partitioning experiment only illustrated the bulk properties of the pesticides despite the choice of two appropriate bulk solvents. Thus, it is more appropriate to view the data as
complementary as opposed to conflicting. It shows the behaviour of the pesticides under slightly different conditions. It will be seen later in the study how both sets can be incorporated in a complete overview of the solubilisation process.

Interestingly, there is only one small cross-peak between the aromatic species and ethoxylate protons which implies that the pesticide is not close to the ethoxylate head groups. Combining this observation with the above result leads to the conclusion that a majority of CP is solubilised in the core.

Another interesting observation in Figure 5.9 is that there are no cross-peaks between the aromatic species and the terminal methyl protons. Instead, there are cross-peaks between the terminal methyl and ethoxylate head groups at about 3.56±0.81ppm as illustrated by Figure 5.11. Observation of these cross-peaks is most unexpected as the terminal methyl group is generally thought to be situated in the very centre of the micelle. Clearly, one cannot justify these cross-peaks as being due to the protrusion of the surfactant tail into the ethoxylate shell as the surfactant molecule would need to be almost completely outside the micelle for this to occur and almost the entire alkyl chain would be exposed to water which is energetically unfavourable. More feasible explanations are that:

1. some surfactants are effectively “solubilised” in the core of the micelle allowing the ethoxylates and the alkyl chain to be in close contact across the chain-ethoxylate interface,

2. some of alkyl chains are bent back on themselves (or bent around the core surface) allowing the terminal methyl to protrude slightly into the shell.

There is currently no other experimental data in literature to support either of these scenarios, but mean field theory simulations did predict the
presence of a small number of surfactant molecules in the cores of micelles as in scenario (1). But this was observed for pure micelles, not solubilised micelles like those studied here. Moreover, scenario (1) would incur a large energetic penalty due to the mixing of polar and non-polar species. In addition, it would mean that the micelles would effectively be solubilising both CP and surfactant molecules themselves, which is not an attractive outcome on the basis of intuition. Indeed if the micelles were capable of solubilising surfactant then one would expect to have observed this particular cross-peak in the pure micellar solution. Scenarios (1) and (2) may need to be more carefully analysed from a vigorous thermodynamic and statistical basis. This approach could be steadily implemented in computer modelling and simulation. The counter-intuitive observation as in scenario (2) where the structural configuration of chains would incur an energetic penalty because of mixing of the non-polar chain in a polar environment could be justified from an overall system energy minimisation by balancing additional entropic gains/penalties associated with the unusual mixing and loss of the flexibility of the alkyl chain.

Figure 5.11- Expanded scale of core-shell interface cross-peaks
A final observation to be made is that the same cross-peaks that were present in the NOESY plot for pure C₁₂E₆ micelles are also present in the C₁₂E₆ + CP NOESY plot, indicating that the overall structure of the core-shell interface is roughly the same in both pure and solubilised micelles. In other words, solubilisation does not affect the main feature of ‘surface roughness’ of the micellar core.

Although it was not possible to obtain NOESY data for C₁₂E₆ + DN the similarities between the partitioning behaviour of DN and CP suggest that DN too is solubilised in the core of the micelles. Identification of both pesticides in the core does, however, have some serious implications on our understanding of the micellar core properties. As discussed in Chapter 2, the most widely accepted view is that the core of a micelle has properties similar to a droplet of pure hydrocarbon since it is almost entirely composed of alkyl chains. In this case, the amount of pesticide solubilised in a micelle should be no more than the solubility of the pesticide in a bulk hydrocarbon. For CP and DN in C₁₂E₆ micelles the maximum solubility’s would be 26 mg per ml of hydrocarbon and 0.032 mg per ml of hydrocarbon, respectively. From the MSR values, however, it was found that the concentrations of CP and DN in the C₁₂E₆ micellar solutions were 0.25mg per ml of micellar solution and 0.12mg per ml of micellar solution, respectively. These values correspond to them having hydrocarbon solubility’s of 780 mg per ml of hydrocarbon and 176 mg per ml of hydrocarbon, respectively. In other words, the hydrocarbon based solubility’s of the pesticides are significantly enhanced by the micelles. The enhancement for CP is a factor of 30 whereas for DN the enhancement is a much more impressive factor of 5500. The micellar environment clearly causes the hydrocarbon to be significantly more efficient at solubilising the pesticides than in the bulk oil.
Since the chemical environments of the different domains in all CₘEₙ micelles are essentially the same the location of CP would presumably be very similar in all of the micelles studied. To verify this, the NOESY plot for C₁₂E₈ + CP was obtained and is shown in Figure 5.12. The same cross-peaks off the diagonal are observed (and circled) as those in Figure 5.9, indicating that the pesticide is also solubilised in the core in these micelles. The lower magnitude of the cross-peaks is attributed to errors introduced during the data processing procedure necessary to produce the 2D plot. A key observation in Figure 5.12 is that there are no cross-peaks between CP and shell protons confirming the pesticide is not in the shell.

5.6.3 ¹H-NMR

Further evidence to suggest the pesticides were solubilised in the core was

![Figure 5.12 - 2D NOESY plot measured for aqueous C₁₂E₆ micelle solution with Cyprodistil. The same two sets of cross-peaks are observed as in Figure 5.9 indicating similar location of CP](image-url)
obtained by analysing the bulk methylene chain peaks in $^1$H-NMR spectra. The methylene peaks are shown for the CP and DN solubilised micelles in Figure 5.13 and 5.14, respectively. Note that there is no spectrum for $C_{12}E_5 + CP$ in Figure 5.13 due to phase separation as has already been mentioned above.

An interesting observation is made in Figure 5.13. It is seen that the methylene peaks of some of the micelles is split into two peaks. For $C_{12}E_8$ and $C_{12}E_{12}$ the peaks are approximately the same size but for $C_{12}E_6$ only a shoulder can be seen to be developing on the right hand side of the main peak and a similar observation is made for $C_{14}E_6$. Only the $C_{10}E_6$ peak has a singlet peak after solubilisation.

The splitting of methylene peaks has been observed in various micellar solutions in the past. Fendler et al. observed this phenomenon in solutions of non-ionic and ionic surfactants with acetophenone and benzophenone. In their study, the splitting was attributed to aromatic shift which is the name given to the effect aromatic substances have on the chemical

![Figure 5.13 - Some $C_mE_n$ micelle methylene peaks are found to split after CP solubilisation](image)

Figure 5.13 – Some $C_mE_n$ micelle methylene peaks are found to split after CP solubilisation
shifts of hydrogens due to their ability to shield protons. It was argued that splitting of a singlet peak occurs due to the partial shielding of only a proportion of the methylene protons. In the cases where the doublet peaks are of equal size it was proposed that approximately half of the methylene groups were shielded. From this the location of acetophenone and benzophenone was determined to be near the core-shell interface of the micelle.

Thus, the observation of peak splitting in the CP solubilised micelles indicates that the pesticide (or at least the aromatic ring) must be in the core of the micelle. The variation in the extent of splitting can be explained by two possible scenarios. Firstly, the higher MSR of CP in C_{12}E_{8} and C_{12}E_{12} simply means that the total amount of shielding is greater in these micelles or secondly, that the shapes of the micelles are such that partial shielding is not plausible in some of the micelles. But regardless of what the actual cause is, the key result is that there is aromatic shifting of at least some of the methylene protons which indicates the presence of pesticide in the core.
Peak splitting is not seen in the $^1$H-NMR spectra of the DN solubilised micelles despite the presence of an aromatic ring in the pesticide. The most likely reason for this is the extremely low solubility of DN in the micelles.

5.7 Micellar Shape Change

Having found that both pesticides caused dehydration of the micellar shell and that both are likely to be solubilised in the micellar core we next investigated what influence the pesticides had on the shape and size of the micelles. In theory, dehydration of the shell should lead to growth of the micelles as is the case when temperature is increased but it is not clear what additional impact the presence of solubilisate in the core might have. SANS was used for this part of the study.

As in the previous chapter, the core-chain model was used to fit the experimental SANS data. The MSR values from Table 5.1 were used to calculate the number of pesticide molecules per micelle and from the above findings all of the pesticide was assumed to be uniformly distributed in the core. By making this assumption it was then possible to calculate the correct scattering length density of the cores which was essential for data fitting.

The SANS experimental data with fitted curves for the C$_{12}$E$_n$ micelles with CP and DN are shown in Figure 5.15 – 5.18 and the data for C$_{10}$E$_6$ and C$_{14}$E$_6$ is shown in Figure 5.19 and 5.20, respectively. The data sets have been translated in the y-axis for clarity. The blue diamonds represent the experimental data for pure micelles, yellow triangles for the micelle + CP system and green squares show for micelle + DN. The corresponding solid curves illustrate the fitted parameters.

Our first observation is that the for the C$_{12}$E$_n$ series, the shorter head group surfactants, i.e., C$_{12}$E$_5$ and C$_{12}$E$_6$, are much more significantly affected by solubilisation of the pesticides than C$_{12}$E$_8$ and C$_{12}$E$_{12}$. In fact, Figure 5.17 and
5.18 show that there is almost no change in the SANS scattering profiles of C\textsubscript{12}E\textsubscript{8} and C\textsubscript{12}E\textsubscript{12} after solubilisation. This tells us that the structural characteristics of the longer head group micelles are barely affected by solubilisation whereas the shorter head group micelles undergo some considerable structural changes. This is interesting given that the MSR values of the pesticides tended to increase with head length (see Table 5.1). This implies that despite solubilising more pesticide (per surfactant) the longer head group micelles are able to maintain the same shape and size.

With regards to the changes seen in C\textsubscript{12}E\textsubscript{5} and C\textsubscript{12}E\textsubscript{6} it is clear that CP has a greater influence than DN. This is most likely due to the higher MSR of CP. Although the magnitude of the change in scattering profile is different for the two pesticides the characteristic changes are actually quite similar. In both cases, there was generally an increase in the gradients of the scattering profiles at low q while the scattering at high q remained essentially the same. This suggests that the structural changes imposed by the pesticides are the same, but just by different amounts. Since the scattering is influenced more strongly at low q it implies that the micelles grew longer but maintained a similar radius after solubilisation. The higher gradient at low q caused by CP suggests that this pesticide caused greater elongation than DN. The changes in micellar properties are more clearly illustrated by the data fitting. The fit parameters for all of the fitted curves in Figure 5.15- 5.18 are given in Table 5.2.
Figure 5.15 – Experimental SANS scattering profiles for C_{12}E_5 (diamond ◊), C_{12}E_5 + DN (square □) and C_{12}E_5 + CP (triangle Δ) with data fittings curves (solid lines). The data has been scaled by a factor of 10 in the y-axis for clarity.

Figure 5.16 – Experimental SANS scattering profiles for C_{12}E_6 (diamond ◊), C_{12}E_6 + DN (square □) and C_{12}E_6 + CP (triangle Δ) with data fittings curves (solid lines). The data has been scaled by a factor of 10 in the y-axis for clarity.
Figure 5.17 – Experimental SANS scattering profiles for C_{12}E_{8} (diamond ◦), C_{12}E_{8} + DN (square □) and C_{12}E_{8} + CP (triangle △) with data fittings curves (solid lines). The data has been scaled by a factor of 10 in the y-axis for clarity.

Figure 5.18 – Experimental SANS scattering profiles for C_{12}E_{12} (diamond ◦), C_{12}E_{12} + DN (square □) and C_{12}E_{12} + CP (triangle △) with data fittings curves (solid lines). The data has been scaled by a factor of 10 in the y-axis for clarity.
Figure 5.19 – Experimental SANS scattering profiles for $C_{10}E_6$ (diamond ◊), $C_{10}E_6 + DN$ (square □) and $C_{10}E_6 + CP$ (triangle Δ) with data fittings curves (solid lines). The data has been scaled by a factor of 10 in the y-axis for clarity.

Figure 5.20 – Experimental SANS scattering profiles for $C_{14}E_6$ (diamond ◊), $C_{14}E_6 + DN$ (square □) and $C_{14}E_6 + CP$ (triangle Δ) with data fittings curves (solid lines). The data has been scaled by a factor of 10 in the y-axis for clarity.
Note that there is no data for C_{12}E_5 + CP in Table 5.2 due to the phase transition in this particular system. The data for C_{12}E_5 + DN, however, was fitted and as predicted the micelles had elongated.

Similar structural changes are observed in C_{12}E_6 with CP and DN. Whereas, two separate curves had to be fitted to the pure C_{12}E_6 micelles, after solubilisation the micellar size distribution becomes narrower, showing that a single set of parameters could be fitted. The solubilised micelles are both

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<th>c (nm)</th>
<th>j (a/c)</th>
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prolate in shape but the CP solubilised micelles are considerably longer than those solubilised with DN. Accompanying this growth is a drastic increase in aggregation number.

For C_{12}E_8 and C_{12}E_{12} solubilisation of CP and DN causes only a slight increase in the dimensions of the micelles and aggregation number. There is no change in micellar shape with both remaining as swollen oblate ellipsoids. CP did have a marginally greater effect than DN but the change is close to the error margin. Figure 5.19 shows that two curves have been fitted to the C_{10}E_6 + CP data. This had to be done because it was not possible to achieve a satisfactory fit with a single set of parameters as was the case with C_{12}E_6. The data, therefore, implies that solubilisation of CP in C_{10}E_6 micelles leads to the coexistence of multiple micellar populations. From Table 5.2 it can be seen that the two fitted curves both correspond to prolate ellipsoids (since \( J < 1 \)) but the micelles described by fit (d) are much longer and thinner than (c).

For C_{10}E_6 and C_{14}E_6 the same trend is observed as above whereby CP has a greater influence on the SANS scattering profiles than DN. This is again attributed to the higher MSR of CP in the micelles. The data fitting for C_{14}E_6 was not as good as the fitting for the other micelles. While it was possible to fit the curves well at high \( q \), the fitted curves were less accurate at low \( q \). The most likely reason for this is that C_{14}E_6 micelles are very long and, therefore, exceed the maximum measurable range in SANS. In this case the long dimension given in Table 5.2 might actually reflect a persistence length for a worm-like structure as opposed to the full length of the micelle. More precise details cannot be obtained from SANS alone for this system.

5.7.1 Characterising Shape and Size Changes

The SANS analysis revealed some interesting features. It showed that in all cases solubilisation of the pesticides caused the C_{n}E_{n} micelles to grow larger.
Additionally, some micelles also underwent shape transformations. With the practical application of micelles in mind these changes can be characterised by relating them to surfactant HLB. Recall the trend between micellar shape and size and surfactant HLB which was illustrated in Figure 4.5. It was found that when HLB < 12 the micelles were prolate ellipsoids. Increasing HLB above 12 led to a rapid reduction in core volume which began to plateau at around HLB = 12.5. At the same time, the shape of the micelles underwent a transition from prolate to oblate ellipsoid. For HLB > 13 the change in core volume became very small and the micelles remained oblate ellipsoid.

Now, by looking at the core volumes and micellar shapes after solubilisation in Table 5.2, it can be seen that the pesticides had the effect of reducing the HLB of the surfactants. For example, the C_{12}E_{6} surfactant has a HLB of 12.5, showing that it is in the transition stage in Figure 4.6. As a result this surfactant adopted various different micellar shapes and sizes. However, after solubilisation of the pesticides the micellar shapes had become prolate and core volume had doubled. These new micellar characteristics resembled those of a surfactant with a lower HLB. Similarly, C_{10}E_{6} has a HLB of 13.3 which is just above the transition range. After solubilisation of CP, however, the micelle was found to have multiple coexisting shapes which implied that the effective HLB of the surfactant had dropped such that it moved into the transition HLB range. The structural changes of the other micelles also follow a similar trend, i.e., a reduction in the effective surfactant HLB.

While this characterisation is convenient from a practical perspective, it must be stressed that it does not carry very much relevance fundamentally. The HLB parameter itself is an empirically determined property and thus has no fundamental significance and its relationship with micellar core volume and shape can only be used for practical purposes. Nevertheless, it is a useful relationship and could prove to be useful in industry.
5.8 Solubilisation Mechanism

In the first part of the study it was found that the pesticides caused the micellar shell to dehydrate. This, therefore, represents the influencing mechanism of the pesticides. In the latter part of the study it was shown that the effect of the dehydration was to cause micellar growth and indeed shape transformation in some cases. The changes had been characterised by proposing that pesticides had caused a reduction in the effective HLB of the surfactants. In essence, what has, therefore, been achieved is a characterisation of the dehydration influencing mechanism. This would allow easier prediction of the influence of any given solubilisate if it also influences micelles via dehydration of the shell. This was one of the main aims of the study and is thus a significant outcome. We finally, propose the following mechanistic solubilisation process that incorporates and explains all the findings in a self-consistent manner.

Initially, when the pesticide is added to the micellar solution it partitions between the hydrocarbon core and hydrated ethoxylate shell at an approximate ratio of 0.3:0.7 as it does in the bulk mixture (Figure 5.8). Due to the presence of hydrophobic pesticide, water is then repelled outward from the palisade layer dehydrating the inner shell region (Figure 5.4). As a result of this dehydration the pesticide begins to favour the hydrocarbon environment (Figure 5.8) and is drawn into the core. This process repeats until equilibration is reached and almost all of the pesticide molecules reside in the core. At this point the inner shell is dehydrated and acts as a barrier ‘trapping’ the pesticide molecules.
The unusually high concentration of pesticides in the core causes the alkyl chains to behave differently from the bulk environment. For example, higher flexibility allows them to bend back and enter the shell as proposed by scenario (2) in Sec 5.6.2. Mixing of the alkyl tail and the inner shell is no longer energetically unfavourable because the inner shell is dehydrated, meaning that this particular arrangement of surfactants and pesticides inside the micelle is entirely feasible. The dynamic and iterative process is schematically illustrated in Figure 5.21.

5.8.1 Time-Dependence of Solubilisation Process

The nature of this mechanistic solubilisation process means that it takes some time to reach completion. This is indeed consistent with our findings from time-dependent SANS measurements which showed almost no structural changes in C_{12}E_6 micelles after 30 minutes of mixing with CP (Figure 5.22) but full transformation after 4 days equilibration time (see. Fig. 5.16)
Similarly, DLS measurements showed a progressive increase in the hydrodynamic radius of C$_{12}$E$_{6}$ micelles while solubilising CP. The measurements were made at one hour intervals and it was found that the micellar system took about 90 hours to reach equilibrium as illustrated in Figure 5.23. Closer inspection of Figure 5.23 indicates that the growth of the micelles actually occurs in two separate stages. The first stage lasts approximately 20 hours and the micelles grow quite rapidly during this period. In the second stage the growth rate of the micelles reduces but the growth continues for nearly 70 hours. Clearly, there must also be a non-growth stage at the beginning of the process as demonstrated by the SANS results, but DLS is not sensitive to this.
5.9 Solubilisation in Other Micelles

The main focus of this part of study was to try to better understand the interactions of pesticides with non-ionic alkyl ethoxylate micelles. This has been achieved quite successfully. As an additional aside, the structural implications of CP solubilisation on ionic SDS and DTAB micelles were also studied. Figures 5.23 and 5.24 show the SANS scattering data for these two systems, respectively. Due to the much higher cmc values of these two surfactants SDS was prepared at 10×cmc and DTAB at 25×cmc.
It was found that CP had no influence on the shape of the scattering profiles of SDS and DTAB implying that there was no structural change in the micelles. The correlation peaks observed in the figures are due to the ionic nature of the micelles and arise from interparticle interactions. As the position

**Figure 5.24 – SANS scattering data for SDS (blue) and SDS + CP (pink) shows CP has very little structural impact on SDS micelles.**

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>MSR</th>
<th>WSR</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{12}-Phosphocholine (zwitterionic)</td>
<td>0.07</td>
<td>0.04</td>
</tr>
<tr>
<td>SDS (anionic)</td>
<td>0.12</td>
<td>0.10</td>
</tr>
<tr>
<td>DTAB (cationic)</td>
<td>0.08</td>
<td>0.03</td>
</tr>
<tr>
<td>C_{12}E_{6} (non-ionic)</td>
<td>0.19</td>
<td>0.10</td>
</tr>
<tr>
<td>C_{14}E_{6} (non-ionic)</td>
<td>0.24</td>
<td>0.11</td>
</tr>
</tbody>
</table>
of this peak did not change after solubilisation either it suggests that CP had no effect on the chemical properties of the micelles either.

Given that CP had no structural impact on the SDS and DTAB micelles it was thought that there would be very little pesticide solubilised in the micelles. But to the contrary $^1$H-NMR results suggested that a reasonable amount of CP had actually solubilised in the micelles (Table 5.3). The MSR of CP in SDS was greater than that in DTAB or dodecyl phophocholine (a zwitterionic surfactant) but in general the MSR in non-ionic micelles was higher. This being said, the WSR of CP in SDS was comparable to that in the non-ionic micelles.

Thus, despite the fact there was CP in the micelles, there was no change in the micellar structure. We propose that the reason for this is that CP influences the micelles via dehydration and while non-ionic surfactants are particularly sensitive to shell hydration ionic micelles are not. Instead, the

Figure 5.25 – SANS scattering data for DTAB (blue) and DTAB + CP (pink) shows CP has very little structural impact on SDS micelles.
The dominant factor determining the properties of these micelles is electrostatic repulsions between head groups.

5.10 Conclusions

Micelles have great potential in formulation technology, but the lack of basic scientific knowledge of underlying principles is hampering technological exploitation. In this work we focussed on assessing the influence of pesticide solubilisates on the size, shape and structure of the micelles, with the ultimate aim of identifying key factors affecting solubilisation. Although solubilisates are well expected to cause structural changes in the micelles it remains unclear why and how they administer these changes. As a result it is still difficult to predict the influence of any given solubilisate on a micellar structure. We studied the solubilisation of two model pesticides, Cyprodinil and Diuron, in C_{12}E_{6} micelles to try to elucidate the mechanistic process from SANS and NMR measurements. SANS results showed that both pesticides caused the micelles to elongate while maintaining an almost constant radius. $^1$H NMR showed that this transformation had occurred due to the dehydration of the micellar shell.

The currently accepted theory of solubilisation predicted that the pesticides would be solubilised in the core due to their medium/ high LogPow values. This was indeed found from NOESY NMR. These observations seem to contradict the observation from the bulk partition experiment between hydrocarbon and hydrated ethylene glycol where it was found that the pesticides preferred to be in the hydrated ethylene glycol partition. However, the solubilisation mechanism proposed not only predicted the conflicting results but also harmonised all the findings of the study. The key factor leading to the observed micellar solubilisation was the shell dehydration which acted as a barrier to trap the pesticides in the core and which enabled an unusually high concentration of pesticides to be solubilised. The high concentration of pesticides in the core-palisade region in turn caused the properties of the alkyl
chains in the core to deviate from bulk hydrocarbon. 2D NOESY revealed a substantially increased extent of intermixing between alkyl chains and ethoxylates as a result of CP solubilisation.
6 Solubilisation in Binary Micelles

6.1 Introduction

Two of the key benefits of this work were outlined in Chapter 1: firstly, to be able to better understand the role of micelles in existing surfactant containing products and secondly, to enable us to use micelles more effectively in new formulations. So far, we have only really addressed the latter since we have only considered “pure” or single component micellar systems. Commercial grade surfactants, on the other hand, generally contain multiple different surfactant structures. Thus, in this final chapter we investigated the properties of binary mixed micelles.

Mixed micelles have in fact received considerable attention over the past few years due to the potential of synergistic effects from mixing surfactants. Examples of such effects include the spontaneous formation of vesicles from mixtures of cationic and anionic surfactants DDAB and SDS despite each individual surfactant only forming micelles normally. Or, in another study it was found that adding DTAB to SDS reduced the cmc of the mixture by over two orders of magnitude. Thus, there is clearly a lot of potential benefit in mixing different surfactants. As a result, much of the work being done in this area involves searching for useful surfactant mixtures. But in this work, our rationale was different. We aimed to investigate the properties of surfactant blends that are obtained unintentionally i.e. in commercial grade surfactants.

The reason commercial surfactants contain different components is due to the high cost of separating each individual component. Thus, while the exact composition of a commercial surfactant will vary from batch to batch, in CmEₙ surfactants the components will generally vary in tail length and head length
about some average. This was illustrated by the chemical analysis of the non-
iononic branched alkyl ethoxylate surfactant Synperonic 13/9 manufactured by
Croda International Plc. The surfactant is advertised as being an isotridecanol
ethoxylate (9) surfactant. However, it was revealed that the surfactant actually
contained a mixture of linear and branched alkyl chains with various degrees
of branching in multiple positions. While the general performance of
surfactants is seemingly unaffected by this kind of mixing the downside is that
it is not known what influence (if any) the mixture will have on the micellar
properties. Therefore, the motivation in this study was to try and understand
whether mixtures of similarly structured surfactants have any synergistic (or
indeed adverse) effects on the solubilisation of pesticides.

Given that the head and tail group lengths can vary in commercial
surfactants it was of interest to study binary mixtures in which both the head
and tail group lengths were changed. Additionally, it was also of interest to
study the mixing of C₁₂E₆ with other surfactants since C₁₂E₆ displayed some
peculiar behaviour. Therefore, four separate surfactant mixtures were studied
in total. For tail length variation C₁₄E₆-C₁₀E₆ and C₁₂E₆-C₁₀E₆ systems were used
and to study the effects of head length variation C₁₂E₁₂-C₁₂E₆ and C₁₂E₆-C₁₂E₈
systems were used. Although the head and tail groups only vary by two units
in the C₁₂E₆-C₁₀E₆ and C₁₂E₆-C₁₂E₈ systems the main motivation for using these
particular systems was to investigate the effects of mixing C₁₂E₆. Moreover, in
the previous chapters it was shown that even such small variation in structure
has significant effects on the micellar properties. C₁₂E₆, for example, was
shown to form multiple different micellar shapes and undergo a significant
transformation after solubilisation. The shape and size of C₁₂E₈ and C₁₂E₁₂, on
the other hand, remained fairly consistent after solubilisation. C₁₀E₆ had an
MSR that was approximately 25% lower than C₁₂E₆ and also showed some
interesting behaviour upon solubilisation. C₁₄E₆ had the highest MSR of all the
surfactants studied but also formed very large micelles under the conditions
they were studied at. Thus, on this basis we expect to see some interesting behaviour in the surfactant mixtures. Throughout the study it was assumed that the micelles are ideally mixed.

### 6.2 Experimental

#### 6.2.1 Materials and Methods

Surfactants were obtained as described in Sec. 4.2.1 but surfactant solutions were prepared at 1%w/v concentration instead of 100xcmc. Three surfactant mixtures at weight ratios, \( \phi = 0.75, 0.50 \) and \( 0.25 \) were prepared for each binary system. For NMR experiments TSP (3-(Trimethylsilyl)propionic-2,2,3,3-d4 acid sodium salt) was added to the micellar solutions at a concentration of 1%w/v as a measurement standard.

Details of SANS and NMR experiments can be found in Sec. 4.2.2.

### 6.3 Micellar Structure

#### 6.3.1 Effect of Mixing Chain Lengths

In Figure 6.1 the SANS scattering profiles for the \( C_{12}E_6-C_{10}E_6 \) mixed micelles are shown. The curves have been aligned in the y-axis to illustrate the variation in the scattering profiles more clearly. It is seen that all the curves have very similar profiles in the high-q range but vary significantly in the low-q range. This illustrates that the smallest dimension of the micelles remains fairly constant while the largest dimension varies. This is consistent with the dimensions obtained for the pure micelles given in Table 5.2. In the figure, the bottommost curve (\( \circ \)) corresponds to pure \( C_{10}E_6 \) micelles and moving up the curves the weight fraction (w.f.) of \( C_{12}E_6, \phi \), increases from 0 to 0.25 (\( \Delta, \) mixture 1), 0.50 (\( \square, \) mixture 2), 0.75 (\( \circ \), mixture 3) and finally 1 (top curve, \( \times \)).
The scattering curves in Figure 6.1 have not been fitted because the exact dimensions of the micelles are not required. Instead, of greater interest is the qualitative change in the physical characteristics of the micelles but this can be inferred by comparing the scattering curves with those of the pure micelles.

As mentioned above, the scattering curves are all essentially the same at high-q but vary at low-q with the curves of the mixed micelles varying within the curves of the pure C_{10}E_{6} and C_{12}E_{6} micelles. This indicates that the physical properties of the pure micelles represent the boundary properties and the mixed micelles have properties somewhere between these. In essence what the curves in Figure 6.1 show is that increasing the wt. of C_{12}E_{6} in C_{10}E_{6} micellar solution causes the micelles to gradually transform from the shape of C_{10}E_{6} micelles to those of C_{12}E_{6} micelles. Interestingly, however, it is seen that the transformation is not linear. For example, in mixture 1 (φ = 0.25) there is quite a significant change in micellar shape from that of pure C_{10}E_{6}. However, when

Figure 6.1 - SANS scattering profiles for pure and mixed micelles. Bottom curve corresponds to pure C_{10}E_{6} moving up the mole fraction of C_{12}E_{6} increases from 0.25 to 0.50, 0.75 and finally 1 (pure C_{12}E_{6}, top curve)
the conditions are reversed in mixture 3 (\(\varphi = 0.75\)) there is almost no change in the micellar shape. The data, therefore, shows that \(C_{12}E_6\) has a much greater influence on \(C_{10}E_6\) micelles than \(C_{10}E_6\) does on \(C_{12}E_6\) micelles.

While it is not possible to determine the exact reason for this from the SANS data a point worth noting is that the cmc of \(C_{10}E_6\) is almost ten times greater than that of \(C_{12}E_6\). This means that in mixture 3 the concentration of \(C_{10}E_6\) is only 8-10x greater than its cmc whereas mixture 1 the \(C_{12}E_6\) concentration is almost 100x its cmc. Thus, although the total concentrations of the two surfactants in the different mixtures were almost the same, their concentrations with respect to their own cmc’s were significantly different. This may contribute to the different influences imparted by the two surfactants. On the other hand, it is also known that the cmc of a surfactant mixture varies from the cmc’s of the pure surfactants the mixture is composed of\(^{105}\) meaning that the fact that \(C_{10}E_6\) was much closer to its cmc value may actually be inconsequential. Indeed given that pure \(C_{12}E_6\) was found to have unique micellar properties it seems more plausible that the former explanation is correct and that \(C_{12}E_6\) has a greater influence on \(C_{10}E_6\) micelles.

The non-linearity in the transformation of micellar properties is unexpected but not really extra-ordinary. It may indicate some element of synergism between the surfactants but in reality the effect is only small. This is an important result in the context of this study since we were specifically looking to see if mixing of the surfactants had any significant influence. The next step was to see if the mixed micelles behaved unusually after solubilisation of the pesticides.

Figure 6.2 shows the SANS scattering profiles of the same set of surfactant mixtures solubilised with CP. As in Figure 6.1 the curves have been arbitrarily aligned to allow more clear illustration of the differences in the curve shapes.
As was the case with the un-solubilised micelles it is seen again that the curves follow almost the same shape in the high-q region but vary at low-q. This time, however, a different trend in micellar shape is observed. Whereas in the un-solubilised systems addition of a small amount of \( C_{10}E_6 \) to \( C_{12}E_6 \) micelles (i.e. mixture 3) resulted in almost no change in micellar properties, after CP solubilisation there was a more significant change in the micellar properties in mixture 3. In fact, mixtures 1 and 3 both adopted similar micellar structures to mixture 2 after CP solubilisation. This departure from the behaviour of the un-solubilised micelles can be interpreted as a demonstration of synergistic behaviour. It shows that in the presence of a solubilisate the different surfactants behave differently such that the shapes of the micelles are fairly consistent regardless of the micellar composition. In the absence of solubilisate the surfactants do not display such behaviour.

The SANS scattering profiles for the DN solubilised systems shown in Figure 6.3 support this conclusion. They show a more linear transformation
from C\textsubscript{10}E\textsubscript{6} to C\textsubscript{12}E\textsubscript{6}. Since the un-solubilised micelles underwent a non-linear transformation the behaviour in Figure 6.3 must also be due to synergistic effects.

Figure 6.4a-c show the SANS scattering profiles for the C\textsubscript{14}E\textsubscript{6}-C\textsubscript{10}E\textsubscript{6} micellar mixtures. The same general features are observed in these mixtures as were seen in the C\textsubscript{12}E\textsubscript{6}-C\textsubscript{10}E\textsubscript{6} mixtures. Firstly, all the scattering profiles follow roughly the same shape at high q, but vary at low q. Next, in the un-solubilised systems when the wf. of C\textsubscript{10}E\textsubscript{6} is low the micellar structure closely resembles that of pure C\textsubscript{14}E\textsubscript{6} micelles but when the wf. of C\textsubscript{10}E\textsubscript{6} is increased the micelles adopt an intermediary structure lying in between those of pure C\textsubscript{14}E\textsubscript{6} and C\textsubscript{10}E\textsubscript{6} micelles. When DN is added to the micellar solutions the structures of the mixed micelles display an almost linear relationship between their structures and the surfactant mixture ratio just as was seen in Figure 6.3. Finally, when CP is added to the mixtures, the micelles tend to adopt a consistent structure which is similar to that of C\textsubscript{14}E\textsubscript{6} + CP micelles.

Figure 6.3 – SANS scattering profiles of mixed micelles with DN
These results demonstrate that having a bigger difference in chain length does not have any significant effect on the behaviour of the surfactant mixtures with regards to their formation of mixed micelles. Moreover, it shows that the presence of C_{12}E_6 does not cause any unusual behaviour despite it displaying unusual characteristics in the pure systems.
Figure 6.4 – SANS scattering profiles for pure and mixed micelles. Bottom curves correspond to pure C_{10}E_{6}, moving up the weight fraction of C_{12}E_{6} increases from 0.25 to 0.50, 0.75 and finally 1 (pure C_{12}E_{6}, top curve) (a) un-solubilised micellar system (b) micellar systems solubilised with DN and (c) CP
6.3.2 Effect of Mixing Head Lengths

Mixing different chain length surfactants resulted in some degree of synergism in that the micelles adopted a fairly consistent structure upon solubilisation of CP. If there was no synergy one would expect a linear transformation of structure as was observed after DN solubilisation. Now we look to see if the same behaviour is observed when mixing different head length surfactants.

Figure 6.5a-c and Figure 6.6a-c show the SANS scattering profiles of the C$_{12}$E$_6$-C$_{12}$E$_8$ and C$_{12}$E$_6$-C$_{12}$E$_{12}$ mixed micellar systems, respectively. Inspection of these figures reveals that the behaviour of these systems is different to those of the mixed chain length systems. It can be seen in the un-solubilised systems (Figure 6.5a and 6.6a) that the mixed micelles have scattering profiles very close to the longer head length surfactant micelles. Only in the C$_{12}$E$_6$-C$_{12}$E$_8$ mixture do any of the micelles resemble C$_{12}$E$_6$ and this occurs when the wf. of C$_{12}$E$_6$ becomes dominant. This is unlike the behaviour observed in the mixed chain length systems above and indicates that the longer head length micellar structures are preferable.

When DN is added to the micellar solutions the structures of the micelles begin to transform but in general they still tend to resemble the structures of the long head length surfactant micelles. When CP is added to the mixed micelles the micelles undergo further structural transformations. However, the systems with high weight fractions of the long head length surfactants still very closely resemble the long head length pure micelles. Once again this behaviour is very different to the mixed chain length micelles.
Figure 6.5 – SANS scattering profiles for pure and mixed micelles. Bottom curves correspond to pure C_{12}E_6, moving up the weight fraction of C_{12}E_6 increases from 0.25 to 0.50, 0.75 and finally 1 (pure C_{12}E_6, top curve) (a) un-solubilised micellar system (b) micellar systems solubilised with DN and (c) CP.
Figure 6.6: SANS scattering profiles for pure and mixed micelles. Bottom curves correspond to pure C_{12}E_{12}, moving up the weight fraction of C_{12}E_{6} increases from 0.25 to 0.50, 0.75 and finally 1 (pure C_{12}E_{6}, top curve) (a) un-solubilised micellar system (b) micellar systems solubilised with DN and (c) CP.
6.4 ¹H-NMR

Although the synergistic behaviour between the mixed chain length surfactants is not as strong as what has been observed in other systems the SANS data presented above clearly showed some degree of synergism occurred. We thus looked to see if ¹H-NMR reflected this behaviour.

Table 6.1 shows the MSR of CP in the C₁₂E₆-C₁₀E₆ and C₁₂E₆-C₁₂E₈ micelles. It was found that the MSR varied linearly with micellar composition for both surfactant mixtures indicating that there was no synergistic behaviour with respect to the solubilisation capacity of the micelles. This is more clearly highlighted by the third and fourth columns in Table 6.1. The third column shows the total mass of pesticide solubilised in the 1% mixed micellar solutions and the fourth column shows the equivalent mass of pesticide that would be solubilised by the surfactants if they were prepared separately. For example, in mixture 4 the weight fractions of C₁₂E₆ and C₁₂E₈ are 0.75 and 0.25 respectively. Thus in a 1% solution the total concentrations of the surfactants are 7.5mg/ ml and 2.5mg/ ml, respectively. The fourth column shows the total mass of pesticides that would, therefore, be solubilised in a 7.5mg/ ml solution of C₁₂E₆ and 2.5mg/ ml solution of C₁₂E₈. Comparison of the third and fourth columns, therefore, allows us to see the influence of the mixed micelles. It is seen that there is very little difference in the values obtained for the mixed micelles and equivalent pure micelles confirming the absence of synergism.

From this data we can conclude that although the SANS data showed synergistic behaviour between C₁₂E₆ and C₁₀E₆ in terms of micellar structure the ¹H-NMR data presented shows that there is no such co-operative behaviour in terms of the micellar solubilisation ability. The same observation was also made for the other head and chain length mixtures.
6.4.1 Micellar Structure

Analysis of the proton peaks in the $^1$H-NMR spectra was able to shed some light on the internal structure of the mixed micelles. Figure 6.7 compares the proton peaks of the ethoxylate head groups in the C$_{12}$E$_6$-C$_{10}$E$_6$ mixed micelles under the various mixture ratios to the peaks in pure micelles (top is for pure C$_{12}$E$_6$ micelles and bottom for C$_{10}$E$_6$). The key observations in the figure are the development of a shoulder on the first and second EO peaks when $\phi = 0.25$ and the eventual splitting of these peaks at $\phi = 0.50$. Given that the chemical shifts of the EO peaks correspond to the specific hydration of the EO units these
observations indicate that the EO units in each of the two surfactants experience slightly different chemical environments. When $\phi = 0.50$ the number of each surfactant is approximately equal, so the EO peaks are split into two peaks of equal size. Since the separation of the two peaks is very small the corresponding change in environment must also be very small. One way in which the splitting could be interpreted is to say that the ethoxylate chains of the two surfactants adopt different conformations. This could indeed cause different EO groups to experience different chemical environments. However, a more probable cause becomes apparent when one looks at the $^1H$-NMR peaks of the surfactant tail as in Figure 6.8.

It is seen in Figure 6.8 that the methyl peak of the un-solubilised mixed micelles is also split into two discrete peaks. This indicates that the methyl protons from the two surfactants are also in unique chemical environments. In this case, however, variations in the tail conformation are a more unlikely cause. A more feasible explanation is that the surfactant alignment is staggered
in the micelle due to the shorter length of the C$_{10}$E$_6$ surfactants. It is seen that
the methyl peak is more broadly split in the C$_{14}$E$_6$-C$_{10}$E$_6$ mixture this is due to
the greater difference in chain length and subsequent larger variation in the
chemical environment of the terminal methyl group.

Interestingly, in the C$_{14}$E$_6$-C$_{10}$E$_6$ mixture the bulk methylene group is
also split. This indicates that the bulk methylenes of the C$_{14}$E$_6$ and C$_{10}$E$_6$
surfactants are also in unique environments. This seems counter-intuitive since
one would expect that the bulk methylenes would be in the same region of the
micelle. However, the observation can be understood if one considers that the
chemical shift of a proton in a $^1$H-NMR spectrum is based on both its position
in a particular molecule and its chemical environment. Thus, whilst the
chemical environments of the bulk methylenes are more or less the same for
both surfactants the positions of the protons with respect to the full surfactant
molecules are different which gives rise to the peak splitting.
The splitting of the peaks is quite a subtle effect but its implications are very useful in understanding the micellar internal structure. For example, in the C\textsubscript{12}E\textsubscript{6}-C\textsubscript{10}E\textsubscript{6} mixed micelles we can say that if the methyl group of the C\textsubscript{10}E\textsubscript{6} surfactants in the centre of the micelle is aligned with the first methylene group of the C\textsubscript{12}E\textsubscript{6} surfactants then the first ether oxygen of the C\textsubscript{10}E\textsubscript{6} surfactants would be aligned with the \(\alpha\)-CH\textsubscript{2} of the C\textsubscript{12}E\textsubscript{6} surfactants as shown in Figure 6.9. As a result of such an alignment both the methyl groups and the first few EO groups for the two surfactants would be in slightly different chemical environments giving rise to the peak splitting observed in Figure 6.7 and 6.8. The observation of peak splitting in only the peaks for the first few EO groups occurs because the extra flexibility of the EO chains in the shell allows the chains to re-configure such that after the first few EOs the environment becomes consistent for the remainder of the EO groups. Likewise in the C\textsubscript{14}E\textsubscript{6}-
C_{10}E_6 mixture the staggering of the surfactants leads to splitting of the terminal methyl group. But due to the larger difference in the chain lengths even the bulk methylene NMR peak underwent peak splitting.

Further evidence to suggest that the surfactants are staggered in the micelles was obtained from NOESY NMR. Figure 6.10 shows the NOESY plot of the C12E6-C10E6 ø = 0.50 mixture. It can be seen that there are two cross-peaks indicating interactions between the terminal methyl protons and the bulk alkyl protons. As these peaks were not observed in the pure C_{12}E_6 NOESY plot it verifies that the surfactants are staggered in the centre of the mixed micelles.

Figure 6.8 also shows that after CP solubilisation the terminal methyl and bulk methylene peaks are no longer split indicating a change in the alignment of the surfactants in the micelles. More specifically it implies that the methyl protons are no longer in different environments as illustrated by the single peak in Figure 6.8. This presumably happens because the surfactant tails
bend away from the centre of the micelle towards the shell as proposed in Chapter 5. In addition to this, however, it is also found that all the EO groups for the two surfactants are found to be in unique environments as opposed to only the first few EO groups as shown by the peak splitting for each of the EO peaks in Figure 6.11. While we can speculate that this is most likely due to the change in shell hydration after solubilisation a more precise description cannot be found from the $^1$H-NMR spectra alone. Nevertheless, it can be seen from the data that there is significant re-structuring of the surfactants in the micelles after solubilisation.

For the C$_{12}$E$_6$-C$_{12}$E$_8$ mixed micelles there is no peak splitting in the methyl peaks due to the fact that the surfactants both have the same alkyl tail lengths, indicating that there is no staggering of the surfactants. Likewise there is no peak splitting of the EO group peaks, again due to the fact the surfactants are not staggered. No unusual behaviour is observed in the $^1$H-NMR spectra after solubilisation either implying that mixing different head length

![Figure 6.11 - $^1$H-NMR spectra of head groups for C$_{12}$E$_6$-C$_{12}$E$_8$ mixed surfactant mixtures after solubilisation of CP](image)

Figure 6.11 - $^1$H-NMR spectra of head groups for C$_{12}$E$_6$-C$_{12}$E$_8$ mixed surfactant mixtures after solubilisation of CP
surfactants has little impact on the internal structuring of micelles.

A key point highlighted by the results presented above is that they demonstrate that despite the fact that micelles are dynamic aggregates with surfactants constantly exchanging between the micelles and bulk solvent, within the micelle the surfactants are rather rigidly aligned. The alignment is such that the methyl protons of different surfactants experience a measurably different chemical environment within the core of the micelle. According to our current understanding of micelles whereby the core is liquid-like in nature and the alkyl chains are able to flex and kink this might not be expected.

6.5 Conclusions

The purpose of this part of study was to determine whether mixing different \( C_mE_n \) surfactants had any impact on micellar formation and their ability to solubilise substances. It was found that mixing of different chain length surfactants did have some synergistic effects with regards to the physical characteristics of the micelles before and after solubilisation. More specifically, it was shown that upon solubilisation of CP \( C_{12}E_6-C_{10}E_6 \) micelles tended to adopt a more consistent shape regardless of the surfactant mixing ratio. Solubilisation of DN, on the other hand, resulted in an almost linear transformation of micellar shape whilst the shape transformation without pesticide displayed more non-linear behaviour. In essence, the data shows that the presence of different surfactant components in a mixture causes surfactants to behave co-operatively allowing for the formation of more structurally stable aggregates.

\(^1\text{H-NMR} \) results revealed some rather precise details about the internal structure of micelles and the alignment of surfactants. It showed that despite the fact that micelles are dynamic structures surfactants are actually aligned
quite consistently in the absence of solubilisates but can also re-align to accommodate solubilisate molecules.

Despite the ability of surfactants to behave co-operatively, however, mixing surfactants of either varying head or tail length did not provide any synergistic properties with regards to solubilisation capacity. At the same time, the data also showed that there were no adverse effects of mixing micelles, which is particularly important in industry due to the impure nature of commercial surfactants.

Variation of the surfactant head group length displayed no unusual or synergistic behaviour.
Micelles possess a number of properties that are potentially very useful in industry. But despite being extensively studied our understanding of micellar science is still incomplete. Micellar solubilisation is an area in particular that requires much further study. As a result of the limited knowledge of micelles, their uptake into industry has been slow and there remain very few commercial products that make explicit use of them.

In this work we have attempted to address three important areas that have both practical and fundamental importance. Firstly, we systematically investigated the relationship between micellar structure and surfactant structure for non-ionic alkyl ethoxylate micelles. One of the key results in this study was the observation of a trend linking micellar core volume and shape and surfactant HLB. Although the empirical nature of HLB meant that the trend did not reveal any fundamental information, it does have potential practical use since it allows the physical characteristics of \( C_{m}E_{n} \) micelles to be predicted fairly easily. Another important result revealed was the coexistence of multiple micellar shapes in \( C_{12}E_{6} \) solution. Indeed, a thorough search of literature showed that this had been reported in the past but the general belief was that the coexistence of multiple micellar shapes was unlikely to occur or only in special circumstances. Not only did our results indicate the coexistence of micellar shapes it was also shown that this observation was consistent with the aforementioned trend with surfactant HLB.

In the next part of the thesis we studied the interactions of two model pesticides, Cyprodinil and Diuron, with the two series of \( C_{m}E_{n} \) surfactants in Chapter 4. It was found that solubilisation generally resulted in the growth of micelles with some micelles being more greatly affected than others and some
also undergoing shape transformations. This finding may have implications on the use of surfactants in size sensitive applications. By relating the shape and size transformations to the micellar core volume-HLB relationship it was seen that the pesticides had the effect of reducing the surfactant HLB.

A combination of NOESY NMR and partition experiments showed that the pesticides had solubilised in the micellar core. From this it was determined that the micelles had enhanced the hydrocarbon solubility of CP by approximately 50 times and DN by a staggering 5000 times. However, although the DN solubility had been much more significantly enhanced this pesticide also had a much lower MSR in the micelles than CP in general.

Analysis of shell hydration showed that the influencing mechanism of the pesticides was via dehydration of the shell. This was consistent with the finding that the pesticides had caused an effective reduction in HLB. Identification of this influencing mechanism also allows for more reliable prediction of the influence of other substances in C_mE_n micelles. Furthermore, the dehydration mechanism fits the time-dependent mechanistic solubilisation process that was proposed for the solubilisation of the pesticides.

Finally, it was shown that solubilisation of the pesticides in two charged micelles did not cause any appreciable change in micellar structure despite the fact that the micelles had solubilised almost as efficiently as the non-ionic micelles (SDS had, at least). This was attributed to the fact that surfactant interactions in ionic micelles are dominated by electrostatic repulsion. Thus dehydration of the micellar shell did not have any significant influence on the micelles.

In the final part of the thesis we turned our attention to binary micelles. Specifically, we studied two mixtures in which the head group length and tail length had been varied respectively. It was found that varying the head group length had little effect on the micelles before or after solubilisation. Mixing
different tail length surfactants, on the other hand, showed some signs of synergistic behaviour. Whereas before solubilisation of the pesticides the transformation of the micellar shape and size with the surfactant mixing ratio was non-linear, after solubilisation the relationship between micellar properties and surfactant composition was much more consistent. Despite this synergistic behaviour, however, the solubilisation capacities of the mixed micelles varied linearly with surfactant mixing ratio i.e. there were no cooperative effects.

$^1$H-NMR results provided precise details on the internal structure of mixed micelles and indicated that in the un-solubilised fixed head length mixed micelles the alignment of the surfactants was staggered. After solubilisation, however, there were no further signs of staggering in the micellar core but instead more extensive staggering in the shell.

Overall the data reported in this thesis has enabled us to paint a fairly detailed picture of $C_mE_n$ micelles and the solubilisation process. But at the same time it has opened up a number of areas for further study such as:

- What are the fundamental conditions required for coexisting micellar shapes? Theoretical studies have fallen short of predicting coexisting shapes but recent experimental and simulation data is suggesting that the occurrence is quite common. Accordingly, it would seem that the thermodynamics of micellisation needs to be revisited to accommodate recent results.

- Why does the enhancement of solubility vary so greatly for different substances? For example, the difference in solubility enhancement of CP and DN is two orders of magnitude.
What are the processes involved in solubilisation in ionic micelles? Since there was no change in the physical properties of the micelles after solubilisation does this mean the core becomes more densely packed?

Our work on two simple binary systems revealed some interesting results which show there is still much to be learned in the field. There is a need for more comprehensive studies.

The above points represent some potential areas for future work which have been drawn directly from the findings of this thesis. But another area that could potentially be of great benefit to micellar science in general is simulation modelling. At one time computer simulations of multi-atomic systems could take days or weeks to perform but with the advent of multi-core CPUs it is becoming possible to perform multi-molecular simulations in a matter of hours. This means that it is now feasible to perform computer simulations of surfactant systems. One of the key benefits of this is that it allows micellar systems to be studied without expensive experimental techniques such as neutron scattering. Moreover, computer simulations could potentially provide more reliable and accurate data since analysis of neutron scattering data usually involves the use of simplified models whereas in simulations the surfactant system can be replicated exactly.

In addition to the availability of more powerful hardware and software advances have also helped to drive this field. In particular, the development of the Single-Chain Mean Field Theory (SCMFT) has been especially useful for studying surfactant solutions and micelles. The basis of this theory is that the behaviour of a molecule in a system can be predicted by analysing the mean field experienced by the molecule that has been produced by a set number of other molecules in a simulation box. For the simulation to work one only needs to input interaction parameters that describe the interactions between different parts of the molecules in the box. While SCMFT has been able to predict cmc
values for various C\textsubscript{m}E\textsubscript{n} surfactants with reasonable accuracy the predictions were obtained by using a simplified ‘bead’ model for the surfactants. The next step is to replace the bead model with actual surfactant parameters and determine the correct interaction parameters such that the shapes and sizes of micelles can be predicted.

One way in which the interaction parameters can be determined is by fitting experimental SANS data with the concentration profiles data obtained from SCMFT simulations. Figure 7.1 illustrates a typical concentration profile for a surfactant micelle obtained using SCMFT. The corresponding rendered micellar structure is illustrated by the inset figure. By varying the input interaction parameters the output concentration profile will vary. Then using the simulated concentration profile with a ‘core-multi-shell’ SANS model it is possible to fit SANS data. The core-multi-shell model is similar to the core-shell model described in Sec. 3.1.3 but instead involves building a

![Figure 7.1](image)

*Figure 7.1- Typical concentration profiles of tail (○), head (□) and water (△) groups in a simulation box as obtained from an SCMFT simulation. (Inset): Rendered image of surfactant micelle from concentration profiles*
mathematical model of a micelle with a core and multiple shells whose contents are determined by the concentration profile. When a satisfactory fit has been achieved the interaction parameters can be determined.

Ultimately, it is desirable to use SCMFT to predict micellar solubilisation. This would be extremely useful because it could help to overcome issues that are restricting the commercial use of micelles currently such as their limited solubilisation capacity. There is still some way to go, however, before this goal is reached.
Bibliography


80. Gracia, C., Gómez-Barreiro, S., González-Pérez, A. & Nimo, J. Static and dynamic light-scattering studies on micellar solutions of


104. Sheehan, O. Investigation of Synperonic 13/9 and 13/8. 6 (Bracknell, 2010).