Physico-chemical Characterisation of Overbased Oil-soluble Phenate Detergents.

A thesis submitted to the University of Surrey in partial fulfilment of the requirement for the degree of Doctor of Philosophy, in the Faculty of Science.

submitted by

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Abstract

This thesis describes an experimental and molecular modelling investigation of calcium carbonate oil soluble detergents. These are used as additives in lubricating oils, mainly to neutralise acidic by-products of the combustion process. Most of the work was carried out for phenate surfactant molecules.

The work has confirmed that the detergent and calcium carbonate form an inverse micelle structure, with the diameter depending on the level of overbasing.

A range of analytical techniques including, gravimetric analysis and spectroscopy assisted by 'ab initio' quantum mechanical calculation has been used to identify the chemical species present in these additives. The results of this work are discussed in chapter 2. Langmuir trough surface pressure and surface tension measurements were made to obtain information on the physical arrangement and surface properties of the overbased particles, the results of which are described in chapter 3. Molecular dynamics simulations on model structures were performed, enabling information on the molecular structure of the micelles to be obtained. These computations showed that the micelles are quite rigid structures, even at engine temperatures and that the phenates are probably discoid shaped, whereas sulphonate micelles are spherical. The bulk properties of the neat additives and in solution were investigated using dielectric spectroscopy, rheology and dynamic light scattering, and provided evidence for weak aggregation of the individual micelles into large clusters. This work is described in chapter 5.

Chapter 6 concludes by bringing together the results from the experimental and modelling studies, presenting the main conclusions and suggesting topics for further research.

Acknowledgements

Firstly I would like to thank my supervisor, Dr. D. M. Heyes for all his help and encouragement throughout the course of this research.

I would like to acknowledge the help given by all the ADIBIS staff, especially Dr. S. Cook, Dr. A. Psaila and Dr. D. Moreton. Particular thanks must go to Dr. J. Crawford (ADIBIS) for his never ending enthusiasm and belief in the project, and to Mr. C. Cane (formerly ADIBIS) for teaching me the 'black art' for synthesising these compounds.

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The University of London Solid-State NMR Unit (University College) is thanked for carrying out the solid-state NMR work. GAUSSIAN92 computations were carried out on a CONVEX C3 at the University of London Computer Centre.
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBN</td>
<td>Total Base Number</td>
</tr>
<tr>
<td>SANS</td>
<td>Small Angle Neutron Scattering</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small Angle X-ray Scattering</td>
</tr>
<tr>
<td>EXAFS</td>
<td>X-ray Absorption Fine Structure (spectroscopy)</td>
</tr>
<tr>
<td>CaPhe</td>
<td>calcium phenate</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet (spectroscopy)</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infra-Red (spectroscopy)</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance (spectroscopy)</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin Layer Chromatography</td>
</tr>
<tr>
<td>RMM</td>
<td>relative molecular mass</td>
</tr>
<tr>
<td>T</td>
<td>temperature in Kelvin</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avagadros number ($= 6.022 \times 10^{23} \text{ mol}^{-1}$)</td>
</tr>
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Chapter 1. Introduction
1.1 Introduction

Lubrication is an essential feature of all modern machinery and has been throughout the ages. The first authenticated use of lubricants is found in the relics of ancient Egypt,\(^1\) where mortar was used as the lubricant for floating the massive stones of the pyramids into place.

Over the years, the advance of engineering technology and the performance requirements of modern engines has placed greater demands on lubricating oils to a point where simple mineral oils are no longer able to protect the moving parts. This is true in almost all applications - industrial, marine, aviation and automotive. Internal combustion engines require effective lubrication to keep the moving surfaces apart. Under these conditions of high temperature and pressure, mineral oils would simply oxidise, thicken and then fail. Another problem is chemical attack of the engine by combustion products - this is especially true in marine applications where the fuel typically has a high sulphur content, giving rise to sulphur acids which are responsible for corrosive wear, and where the engines often operate continuously for several weeks.

To overcome this degradation a range of 'additives' are mixed with the mineral oil. Additives capable of improving the properties of lubricating oils were first used around 1850,\(^2\) and since then demand has grown as they have been tailored to achieve the required level of oil performance without entailing excessive cost. Figure 1.1 shows the engine lubrication system for a typical internal combustion engine.\(^3\)
Additives are defined as chemicals that are mixed as minor components to lubricating oils to enhance existing natural properties, or in some cases to provide new properties. Modern lubricants are complex mixtures containing many different chemical components. The types of additive included depend largely upon the service for which the oil is required. The main types of additive include dispersants, detergents antiwear agents, antioxidants, Viscosity Index (VI) improvers, friction modifiers and pour point depressants. One of the most important classes of additive is the detergent which is the subject of this thesis.

The lubricant additive industry spends $400 million each year on research & development. The world-wide industry has a turnover of $4000 million per annum, of which the European market comprises one third. Since the 1930s when crankcase lubricants contained no additives, internal combustion engines have become more sophisticated, which has stimulated the need for the development of additives. Today's lubricants contain 10-20% additives. Figure 1.2 shows how additives have evolved over the last 70 years. The year in the graph indicates when each type of additive chemical was introduced.
Figure 1.2 Development of additives

The development cost of a single lubricant can be as high as $600,000, as rigorous engine tests are required. Lubricants contain a variety of different additives which can comprise up to 5% of the finished oil. Table 1.1 shows two different additive packages.

Table 1.1 Additive packages for passenger car oils and marine oils

<table>
<thead>
<tr>
<th>Additive type</th>
<th>Passenger Car</th>
<th>Heavy duty diesel/Marine</th>
</tr>
</thead>
<tbody>
<tr>
<td>dispersant(%)</td>
<td>52.2</td>
<td>37.0</td>
</tr>
<tr>
<td>detergent(%)</td>
<td>27.2</td>
<td>34.4</td>
</tr>
<tr>
<td>antiwear(%)</td>
<td>13.0</td>
<td>13.0</td>
</tr>
<tr>
<td>others(%)</td>
<td>7.6</td>
<td>15.7</td>
</tr>
</tbody>
</table>
1.2 The Combustion Process

The internal combustion engine generates power by converting chemically bound energy into work by the use of reciprocating motion. The burning of fuels releases energy in the form of heat causing a pressure to rise in the combustion chamber, which is then converted into mechanical energy. (Figure 1.3)

\[
\text{FUEL} + \text{OXYGEN} \rightarrow \text{CARBON DIOXIDE} + \text{WATER} + \text{ENERGY}
\]

(Figure 1.3 Generation of energy)

However, sulphur compounds present in the fuel oxidise to form sulphur oxides during this process, which then react with water (also a by-product of combustion) to form sulphur acids (e.g. $\text{H}_2\text{SO}_4$), which can be significant in diesel engines where the fuel contains up to 5% sulphur.

\[
2\text{SO}_2(g) + \text{O}_2(g) \leftrightarrow 2\text{SO}_3(g)
\]

\[
\text{SO}_3(g) + \text{H}_2\text{O}(l) \leftrightarrow \text{H}_2\text{SO}_4(l)
\]

There are also oxy-acids which result from the oxidation of lubricant base oil and fuel fragments. Base oil is a complex mixture of aromatic, paraffinic and naphthenic components, with some sulphur and nitrogen containing compounds. Analysis has shown that the mixture of soluble and insoluble compounds appearing as a result of oil oxidation includes, amongst others, nitrous and sulphur oxides. These products are corrosive and cause degradation of the oil, resulting in deposits forming on engine parts, and an increase in the viscosity of the oil. A range of additives is therefore
required to overcome these adverse reactions and which are discussed in the following section.

1.3 Additives

As mentioned earlier, additives can comprise up to 15% by volume of a typical lubricant. A brief description of a number of additives is given below.

1.3.1 Dispersants

Oil viscosity problems resulting from high levels of insolubles in the oil, can be overcome by the addition of dispersant additives to the oil. The sludge and varnish-forming precursors, resulting as by-products of the fuel combustion process, contaminate the engine oil as they blow by the piston rings into the engine crankcase. Prior to the introduction of dispersants, these contaminants would settle out on critical parts of the engine thereby hampering its operation. Dispersants are usually high molecular weight compounds such as polyisobutenyl succinimides.

Mode of action}

Mode of action5

\[
\text{Sludge} + \text{Dispersant} \rightarrow \text{Sludge micelle}
\]
Chapter One: Introduction

The polar head of the dispersant interacts with the sludge particle, whilst the tail keeps it soluble in the oil.

1.3.2 Antiwear/ Antioxidants

These types of additive work by adsorbing onto metal surfaces at working temperatures. These layers are then wiped off in preference to the metal surface, when contact occurs thereby minimising the damage to the metal surface. The action of a typical anti-oxidant is shown below.

<table>
<thead>
<tr>
<th>Mode of action</th>
</tr>
</thead>
<tbody>
<tr>
<td>OIL → Air → Heat</td>
</tr>
<tr>
<td>RADICALS, PEROXIDES → DEPOSITS SLUDGE ACIDS</td>
</tr>
<tr>
<td>good antioxidant system</td>
</tr>
</tbody>
</table>

1.3.3 Viscosity Index (VI) Improvers

The viscosity of a lubricating oil varies with temperature, i.e. at high temperature the viscosity is reduced. At low temperature during engine start-up, the viscosity must be relatively low, yet at high temperature when the engine has been running for some time, the viscosity must be sufficiently high for the oil to act as an effective lubricant. The dependence of the viscosity with temperature is known as the Viscosity Index. Generally a high viscosity index is desirable which results in a small change in the viscosity with temperature.
Viscosity Index improvers are additives that modify the viscosity characteristics of the oil. Polymethacrylates (PMS) and Olefin co-polymers (OCP) are viscosity index improvers. At low temperatures they exist as random coils, which then unravel at higher temperatures resulting in an increase in the viscosity of the oil.

Mode of action

1.3.4 Friction Modifiers

Following the demand for greater fuel economy, chemicals were needed that reduced the friction between the metal surfaces in engines. Products such as graphite, fatty esters and molybdenum disulphite were used as additives. These additives work by lowering the internal friction inside the engine, therefore limiting the power loss.

1.3.5 Pour Point Depressants

Most paraffinic oils (even after refining) contain wax which will come out of solution at low temperatures to cloud the oil and in some extreme cases solidify it. Pour point depressants are additives that modify the wax crystals thus enabling the oil to flow. Polymethacrylates are common pour point depressants.
1.3.6 Detergents

Incorporation of detergent additives into modern lubricants is essential to prevent harmful carbon and sludge deposits, which can accumulate in critical areas of the engine causing it to fail. The basic functions of a detergent additive are:

1. Neutralisation of corrosive acids

2. To minimise oil thickening thereby maintaining viscosity stability and flow properties.


Detergents provide cleaning action in engine oils by neutralising acids which arise from fuel combustion products, namely sulphur acids, nitro acids and oxy acids.

Colloidal dispersions of inorganic carbonates are known to fulfil all of these requirements. The detergent polar substrate is made up of two parts shown schematically in Figure 1.4. The hydrocarbon chain (oleophilic (oil-loving) portion), is the portion of the molecule that enables the detergent molecule to be soluble in the base oil. The polar head group is negatively charged, forming an ion pair with a cation (usually Ca$^{2+}$).

![Figure 1.4 Detergent Polar Substrate](image)

Hydrocarbon Tail
Oleophilic Group
Solubiliser

Polar Head
Metal Attachment Point
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The evidence to date is that these overbased detergents take the form of an inverse micelle, with the surfactant forming a shell around a core of calcium carbonate. Reverse micelles form in apolar solvents from amphiphilic molecules whose polar heads occupy the core of the structure and the hydrocarbon chains extend outwards into the surrounding solvent. The classical inverse micellar system is sodium bis(2-ethylhexyl) sulfosuccinate (AOT), the structure of which is shown in Figure 1.5. The AOT systems differ greatly from these overbased systems in that they have a core of water molecules as compared to inorganic carbonate. These particles are much larger than the overbased additives, having a core radius of typically up to 200Å.

![Figure 1.5 Structure of sodium bis(2-ethylhexyl)sulfosuccinate (AOT)](image)

These types of inverse micelle have several novel aspects related to their structure. For example, they have the ability to solubilise macromolecules such as proteins in the micro-aqueous phase, and they can also be used as micro-reactors for the synthesis of a variety of materials (e.g. polymers), and for gas hydrate formation, which has important commercial implications. An interesting feature of these AOT systems is that the micelle core radius, \( R \), can be related to the water-to-surfactant molar ratio, \( \omega_0 \), by the following equation:

\[
R = 1.5\omega_0
\]

In chapter three it is shown that for the overbased phenate detergent systems, the core radius can be related to the carbonate-to-surfactant ratio by a factor of 0.3.
Detergent Types

Lubricant detergent additives are an association of two distinct chemical species:
1. A metal surfactant salt.
2. A store of inorganic base.

Neutral detergents contain only the surfactant component, whereas 'overbased' detergents contain an inorganic base stabilised by the surfactant. The term 'overbased' refers to the fact that these materials contain a stoichiometric excess of base.

The detergents used fall into the following chemical classifications: Sulphonates, phenates, salicylates, phosphonates and naphthenates.

The neutral detergent itself can be synthesised by a simple acid/base reaction. The reaction is represented as:

\[ 2R - H + M(OH)_2 \rightarrow R - M - R + 2H_2O \]

Figure 1.6 Acid/Base reaction for the production of neutral detergents

These detergents can be overbased using the above acid/base reaction, by adding a chemical excess of base (i.e. \( M(OH)_2 \)) to the neutral detergent system. A more common procedure (Figure 1.7), however, is to convert the excess inorganic base into metal carbonate by bubbling in carbon dioxide ('carbonation') into a hydrophobic medium containing the surfactant. The carbonate so formed is stabilised by the surfactant so that it is soluble in oil.
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\[ 2 \text{R-H} + n \text{M(OH)}_2 \xrightarrow{(n-1) \text{CO}_2(g)} \text{R-M-R (n-1) MCO}_3 + (n+1) \text{H}_2\text{O} \]

Figure 1.7 Scheme for the production of overbased carbonates

These detergent additives are thought to exist as inverse micelles, with calcium carbonate in the core and the surfactant in a shell around this core.\textsuperscript{15,16,17} The mechanism of the synthesis will be discussed in further detail in Chapter 2.

**Detergent Classification**

Overbased substrates are defined by the amount of total basicity contained in the product. In recent years it has become increasingly popular to label a detergent by its TBN (total base number). Base number is defined in terms of the equivalent amount of potassium hydroxide in the material. For example a 300 TBN sulphonate contains base equivalent to 300 milligrams of potassium hydroxide per gram (300 mg KOH/g). Different surfactant types can have different TBN values as shown in Table 1.2

**Table 1.2** Range of typical detergent additives

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sulphonates</th>
<th>Phenates</th>
<th>Salicylates</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TBN</strong></td>
<td>0-500</td>
<td>50-300</td>
<td>50-300</td>
</tr>
<tr>
<td><strong>Metal cation</strong></td>
<td>Ca, Mg, Na, Ba</td>
<td>Ca, Ba, Mg</td>
<td>Ca, Mg</td>
</tr>
</tbody>
</table>

Some details specific to each surfactant type are given below.
Sulphonates

Sulphonates are the most widely used detergents. In addition to detergency they also provide excellent anti-rust properties.

Two sources of sulphonate are used, petroleum sulphonates and synthetic sulphonates. The petroleum sulphonates are the so-called 'natural' sulphonates and occur as a by-product in the manufacture of white oil. The synthetic sulphonates are prepared from a synthesised alkyl aromatic substrate (Figure 1.8) and have a variety of structures. For example, if benzene is alkylated by olefin under catalytic conditions, an alkyl aromatic compound is formed. This is then reacted with sulphur trioxide to form the synthetic sulphonic acid.

![Diagram of synthetic sulphonate production](image)

**Figure 1.8** Scheme for the production of synthetic sulphonates.

Both the natural and synthetic sulphonates fall into two general types: neutral and overbased. One advantage of the overbased sulphonates is their ability to neutralise
acidic moieties. The formation of overbased sulphonates is given in Figure 1.9 and is a complex reaction between the neutral species and a metal hydroxide which takes place using carbon dioxide in the presence of a promoter. The promoter acts to dissolve the metal hydroxide, and bring together the reaction components to form a metal carbonate.

\[ RSO_3^\text{neutral}_M + MOH \xrightarrow{\text{promoter, CO}_2} RSO_3^\text{overbased}_M \neq xMCO_3 + H_2O \]

Figure 1.9 Scheme for the formation of overbased sulphonates.

The sulphonate systems have been extensively studied. Previous work on these systems has involved the use of Small Angle Neutron Scattering (SANS) to obtain the particle sizes. Using a mixture of toluene in the H- and D- forms it was possible to obtain a coherent length density of the dispersion medium that matched the core and surfactant layer hence enabling the shell thickness and core diameter to be determined. Calcium carbonate dispersions stabilised by an alkyl-aryl sulphonic acid shell were studied using the technique adopting the concentric sphere approach. These surfactants consist of highly branched chains between C\textsubscript{15} and C\textsubscript{36}. Core sizes of 2.2 and 6.7 nm were obtained, and a shell thickness of 1.9 nm was derived. Other morphological aspects of these particles have been studied by Transmission Electron Microscopy.\textsuperscript{18} EXAFS spectra show that the core is made of amorphous calcium carbonate, the calcium ions being surrounded \textit{ca.} 6 oxygen neighbours at 0.24 nm.\textsuperscript{19} Electrophoretic study of these systems has shown that the particles can carry an appreciable electrostatic charge,\textsuperscript{20} arising from a dynamic equilibrium between the surfactant in the detergent particle and in the solvent.
Phenates

The acidic organic substrates for the phenate are alkylphenols and sulphurised alkylphenols. The olefin used to alkylate phenol may be branched or linear and is generally of average chain backbone length C₉ or greater. The average number of sulphur atoms per sulphur bridge is more than one. This substrate is then reacted with the correct quantity of metal base (and CO₂) to produce the neutral (overbased) detergent. This reaction scheme is summarised in Figure 1.10.

\[
\begin{align*}
\text{OH} & \ + \text{OLEFIN} \\
 & \downarrow \\
\text{ALKYLATION} & \\
\text{OH} & \ \\
\text{ALKYLPHENOL} & \downarrow \\
R & \\
\text{SULPHURISATION} & \\
\begin{bmatrix}
\text{OH} \\
\text{S}_{\times} \\
\text{OH} \\
\end{bmatrix} & \text{SULPHURISED ALKYLPHENOL}
\end{align*}
\]

Figure 1.10 Sulphurised Alkylphenol Production

Compared to the sulphonate systems little similar characterisation has been performed for the phenate detergent types, and the published literature on these is quite small. Structurally they are quite different from the sulphonates, as the stabilising surfactant is
bidentate with a metal salt of the MX type rather than MX$_2$ type (monodentate sulphonate). The surfactant anion is a bidentate ligand consisting of a sulphur bridged phenate. Generally the sulphonates are larger than the equivalent phenate because of their long chain length.\textsuperscript{3} Again the structure of the phenates is thought to be of the form of an inverse micelle, with the carbonate at the core, stabilised by an outer shell (see Figure 1.11). The thickness of the outer shell is typically greater in the case of sulphonates because the alkyl chain is longer.

![Figure 1.11 Reverse micellar structure of phenate](image)

However the ability of the phenate to achieve the same level of stabilisation could be a consequence of the bridged units which will confer unique geometrical constraints on the particle. Ruckenstein argued that non-aqueous dispersions are better stabilised using branched alkyl chains, with two chains per surfactant molecule being more effective than one.\textsuperscript{21} These molecules bound to the surface of the particle possess side chains far from the head group which will keep the particles apart and simultaneously generate enough free space between the surfactant chains to be filled with the liquid medium. This causes the Hamaker constant of the shell to be near that of the liquid medium, reducing the attraction between the particles.
Salicylates, Phosphonates and Naphthenates

The structures of these three detergent substrate types are given in Figure 1.12

![Structures of Salicylates, Phosphonates, and Naphthenates](image)

**Figure 1.12 Typical structures of salicylates, phosphonates and naphthenates.**

The substrates used for the production of metal salicylate detergents are alkyl salicylic acids, which are derived from phenols by the 'Kolbe-Schmitt' reaction (see Figure 1.13). The resulting metal salicylate is converted to an alkaline earth salt by metal exchange with an alkaline earth halide salt.

![Kolbe-Schmitt Reaction](image)

**Figure 1.13 Kolbe-Schmitt reaction for the production of salicylic acid**
A common substrate for phosphonates is produced by the reaction of polyisobutene with phosphorous pentasulphide, the metal usually used being barium (Figure 1.14).

![Diagram of phosphonate production](image)

Naphthenates are generally derived from naphthenic acid substrates.

The chemical class of overbased detergent sold depends largely on the availability of an economic source of starting chemicals. All of the above classes have very similar performance characteristics, determined by the TBN number, rather than the chemical nature of the surfactant.
1.4 Aims of Project

The work reported in this thesis sought to gain a greater understanding of the chemical composition and microscopic structure of the phenate detergent systems. Any advances in our knowledge of these systems may lead the way to improved commercial products. Characterisation of the phenate detergent systems can be separated into the following categories.

Chemical composition

There is a need to determine the chemical composition of the phenate, and this is dealt with in chapter 2. A number of different spectroscopic techniques were employed to identify the chemical species present in the phenate. Fourier Transform Infra Red (FTIR), Ultra Violet (UV), $^{13}$C Solid State Nuclear Magnetic Resonance. Help in interpreting the spectra was obtained using GAUSSIAN92, an *ab initio* molecular electronic structure package.

Microstructural composition

After determining the chemical composition, it is necessary to establish the physical arrangement of the chemical constituents.

Chapter 3 investigates the surface properties of phenate detergents using the techniques of the Langmuir Trough and Surface Tension measurements. The Langmuir Trough technique provides a measure of the size, the interaction potential, and the hydrophobicity of the particles. Surface tension can also provide information on the hydrophobicity of these particles.
Chapter One: Introduction

Having determined the nature of the particles, I sought to determine the physical states of the detergent particles in solution, *e.g.* do they associate?, what is the effect of solvent? Chapter 5 considers the bulk properties of the detergent solutions, in particular the level of aggregation of the particles, by the use of dielectric spectroscopy, rheology and dynamic light scattering.

On the theoretical side, atomistic computer simulation was performed in an attempt to gain a greater understanding of the microscopic structure of these detergents, and is dealt with in chapter 4. This rapidly evolving technique can generate model atomistic structures for these molecules. The results from experimental work were used as input parameters for the modelling work, thus making the simulation model as relevant to the real system as possible. This is the first time this technique has been applied to overbased detergents. Computer simulations were used to help resolve some of the issues that remain concerning their structure. For example,

- Are they spherical micelles?
- What effect does chain length and structure have on the effectiveness of the surfactant molecule to stabilise the carbonate core?
- How is the core structured?
- Does the structure alter significantly in the presence of solvent?
- How do these phenate detergents differ from other types of detergent *e.g.* sulphonates?

Although the work contained in this thesis has gone some way to resolving these unanswered questions, it has highlighted further issues that need to be addressed and these are discussed in Chapter 6.
Chapter 2. Synthesis & Chemical Characterisation
2.1 Introduction

Any commercial product has poorly defined starting components that would limit the effectiveness of any characterisation programme of work. Therefore a number of model phenate overbased detergents were synthesised with better defined starting materials under more controlled conditions, with which detailed analyses could be performed. Compounds of different base content were synthesised which were better defined than any commercial product and therefore more suitable for a detailed investigation.

The conventional scale of overbasing (i.e. the amount of alkaline detergent in the oil) is called the Total Base Number (TBN). The TBN was determined using an industry standard method that determines the basic components by titration with perchloric acid in glacial acetic acid. The base number calculated is defined as the quantity of perchloric acid (expressed in terms of the equivalent number of milligrams of potassium hydroxide) that are required to titrate 1g of the sample dissolved in the specified solvent to a well-defined inflexion point as specified by the test method.

A range of overbased detergents were synthesised at TBN levels of 150, 250 and 300. The procedure for each synthesis was essentially the same, differing only in the ratio of components in the starting mixture. A number of spectroscopic techniques were used in order to identify the chemical species present in these overbased detergent additives. Ultra violet, infra-red, and nuclear magnetic resonance (NMR) were used.
2.2 Synthesis

Alkylphenol is the main starting component in the synthesis of these overbased detergent systems. While the aryl part of the molecule is uniquely defined, the nature of the alkyl chain, even in the model compounds, is still somewhat poorly specified. The synthesis procedure of the alkyl moiety, from propylene tetramer, leads to a product that is probably a mixture of isomers. However, it is reasonable to assume that the most likely product is as described in the cationic polymerisation procedure below, shown in scheme 1.24

Scheme 1

\[
\begin{align*}
\text{CH}_3\text{CH} = \text{CH} + \text{H}^+ & \xrightarrow{\text{CH}_3\text{CH} = \text{CH}_2} \text{CH}_3\text{CH} = \text{CH}_2 \\
\text{CH}_3 & \xrightarrow{\text{CH}_3\text{CH} = \text{CH}_2} \text{CH}_3\text{CH} = \text{CH}_2 \\
\text{CH}_3 & \xrightarrow{\text{CH}_3\text{CH} = \text{CH}_2} \text{CH}_3\text{CH} = \text{CH}_2
\end{align*}
\]
This chain then attaches itself in the *para* -position on the phenol ring, and this is illustrated in Scheme 2.

Although the resulting product is predominantly *para*-substituted, there is some evidence of *ortho* -substitution also.

The synthesis of the overbased detergents is divided into five stages:

A. Sulphurisation of alkylphenol in the presence of lime and ethylene glycol, with the evolution of H₂S;
B. Reaction of the sulphurised alkylphenol with lime during which water is generated;

C. Reaction of the mixture from stage B with carbon dioxide;

D. Removal of ethylene glycol at high temperature and low vacuum;

E. Filtration of the product.

Details of the procedure are given below:

1. An empty 5-necked, 1L reaction flask was weighed.

2. Alkylphenol, lime, lube oil, sulphur, 2-ethyl-hexanol and calcium acetate were added to the flask in the quantities given in Table 2.1. The mixture was then stirred and heated to 145 °C at 700 mm Hg vacuum pressure.

3. Once the temperature had stabilised, ethylene glycol was added dropwise from a dropper funnel, whilst the temperature was raised gradually to 165 °C, (care was taken to avoid adding the ethylene glycol too quickly) and held under these conditions for 1 hour.

4. After 1 hour the vacuum was released, and carbon dioxide (derived from cardice) was bubbled through the reaction mixture at 165 °C, after which time the vacuum was reconnected and the temperature increased to 245 °C. The reaction mixture was kept at these conditions for a further 30 minutes.

5. The pressure was then reduced to 10 mm Hg to complete the removal of unwanted solvents.

6. After 30 minutes, the reaction was cooled to 160 °C, the vacuum released, and the flask was weighed.
7. The product was then vacuum filtered at 140-160 °C using a No.1 sintered glass funnel and a 500 ml Buchner flask (both preheated), packed with a filter aid (a diatomaceous earth).

The stages in the synthesis procedure are illustrated in Scheme 3.

Scheme 3
It should be noted that the sulphurisation takes place in the *ortho-* position to the phenol group. This is because the -OH group is powerfully *para-* or *ortho-* directing towards electrophiles like sulphur, and as the *para-* position is already taken, the sulphur attaches itself at the *ortho-* position. The role of the ethylene glycol is not known but it could act to bring the calcium hydroxide and phenol together prior to carbonation in a favourable state for micellisation.

The structures of the alkylphenol and the phenate surfactant chain are therefore assumed to be those shown in Figure 2.1.

![Figure 2.1 Structure of alkylphenol and phenate](image)

The structure of the phenate shown in Figure 2.1 is a model structure showing only one sulphur atom in the bridge, whereas there may be more than one sulphur atom in this bridging unit, which may be highlighted by spectroscopic analysis.
Table 2.1 Quantities of starting materials

<table>
<thead>
<tr>
<th>TBN</th>
<th>150</th>
<th>250</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkylphenol (g)</td>
<td>147.00</td>
<td>147.00</td>
<td>147.00</td>
</tr>
<tr>
<td>Ca(OH)$_2$ (g)</td>
<td>31.00</td>
<td>66.00</td>
<td>75.00</td>
</tr>
<tr>
<td>Lube oil (g)</td>
<td>129.00</td>
<td>129.00</td>
<td>129.00</td>
</tr>
<tr>
<td>Sulphur (g)</td>
<td>21.00</td>
<td>21.00</td>
<td>21.00</td>
</tr>
<tr>
<td>2-ethyl hexanol (g)</td>
<td>31.00</td>
<td>31.00</td>
<td>31.00</td>
</tr>
<tr>
<td>Calcium acetate (g)</td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
</tr>
<tr>
<td>Ethylene glycol (g)</td>
<td>37.00</td>
<td>37.00</td>
<td>37.00</td>
</tr>
<tr>
<td>CO$_2$ (cardice) (g)</td>
<td>11.00</td>
<td>23.00</td>
<td>26.00</td>
</tr>
</tbody>
</table>
2.2.1 Analysis

The three compounds were submitted for full analytical testing. The results are given in Table 2.2 below.

Table 2.2 Analytical Results

<table>
<thead>
<tr>
<th></th>
<th>TBN 150</th>
<th>TBN 250</th>
<th>TBN 300</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Calcium</td>
<td>5.6</td>
<td>9.6</td>
<td>10.8</td>
</tr>
<tr>
<td>% Sulphur</td>
<td>3.2</td>
<td>3.3</td>
<td>3.4</td>
</tr>
<tr>
<td>% CO₂</td>
<td>3.1</td>
<td>6.2</td>
<td>7.1</td>
</tr>
<tr>
<td>TBN</td>
<td>153</td>
<td>265</td>
<td>299</td>
</tr>
<tr>
<td>Viscosity at 100°C</td>
<td>61</td>
<td>218</td>
<td>402</td>
</tr>
<tr>
<td>(cSt)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Ca incorporated</td>
<td>95.85</td>
<td>94.5</td>
<td>96.06</td>
</tr>
</tbody>
</table>

The viscosities were measured using an Ostwald viscometer (Figure 2.2). The principle of which is as follows. Sufficient liquid is introduced into the viscometer for the levels to be at B and C. Liquid is then drawn up into the left hand side until the liquid level is above point A. The liquid is then released and the time taken for the meniscus to pass between A and B measured. The viscosity, \( \eta \), can then be obtained using the relation, \( \eta = k \rho t \), where \( \rho \) is the density, \( t \) is the time and \( k \) is the viscometer constant determined using a reference fluid whose viscosity is known at that temperature.
Using these results, the ratios of the various components were estimated assuming that there are two types of salt present in the additive i.e. calcium phenate (CaPhe) and calcium carbonate (CaCO\textsubscript{3}). The ratio was calculated on the basis that the number of moles of carbon dioxide bubbled through was equal to the number of resulting CaCO\textsubscript{3} moles in the core. This is a reasonable assumption since over 95% of the CO\textsubscript{2} bubbled in was incorporated into the final product. This percentage was calculated using analytical results for the amount of CO\textsubscript{2} present in the final product, which was then compared to the quantity of CO\textsubscript{2} that was bubbled in. Assuming that the mass of the product contained the same amount of base oil as the starting mixture, the mass of the phenate can be calculated by the difference.

For the 150, 250 and 300 TBN products, the molar ratios were calculated to be 1:1, 1.67:1 and 2:1 respectively. The molar ratio [CaCO\textsubscript{3}]/[Ca(Phe)\textsubscript{2}] was found to be linear with TBN (see Figure 2.3).
Figure 2.3 Molar ratio $\text{CaCO}_3$/Ca(Phe)$_2$ vs. TBN

2.2.2 Isolation of the active species from the oil

The viscous nature and dark colour of these detergent additives made them unsatisfactory for physical measurements. It was therefore necessary to isolate the active components from the base oil by the procedure described below.$^{27}$

Acetone precipitation removes the base oil, and also any unreacted alkylphenol.

a. 50g of the additive was dissolved in 100 ml of n-heptane, which was then added with stirring to a beaker containing 700 ml of acetone.
b. A pale-yellow gelatinous precipitate formed which rapidly flocculated and settled. This was then allowed to stand for several hours. The sediment and supernatant were separated by decantation.

c. The sediment was dried at 85° C to constant weight and then ground in a mortar, forming a yellow powder.

The overbased phenates are manufactured from a starting material comprising mainly of para- dodecylphenol, along with some ortho- and di-dodecylphenol, a small proportion of which remains unreacted in the final product. Previous HPLC analysis has shown that this removes any unwanted starting chemicals from the adduct.28
2.3 Spectroscopic Characterisation

A range of different spectroscopic techniques was employed to characterise and identify the chemical species in these products,

1. Ultra-Violet spectroscopy (UV)
2. Fourier Transform Infra-red spectroscopy (FTIR)
3. Nuclear magnetic resonance ($^1$H, $^{13}$C solution, & $^{13}$C Solid-State NMR) spectroscopy.

*Ab initio* quantum mechanical calculations were also used to help interpret the measured spectra.

*Ab Initio Methods - GAUSSIAN92*

In order to determine the interaction of electromagnetic radiation with these molecules, the coupled motion of the electrons and nuclei needs to be solved using the Schrodinger equation. An exact solution for the many electron-nuclei systems of interest here, is as yet not practicable. A solution with minimum of approximations, called the 'ab initio' approach, is implemented in the quantum mechanics package GAUSSIAN92. Assignment of the UV and FTIR spectra was assisted using the GAUSSIAN92 quantum mechanics package. The basis set used for the UV work was the 6-31G* with HF/CIS and geometry optimisation. The optimised structure obtained was then used in the calculation of the IR frequencies under similar conditions. In accordance with usual practice, the computed frequencies were multiplied by a factor of 0.9 in order to correct for the unrealistic state of the dissociated molecule within the Hartree-Fock approximation.
2.3.1 Ultra-violet spectroscopy

Ultra violet (UV) radiation is the part of the electromagnetic spectrum beyond the violet end of visible light, and encompasses the region between 25000 to 50000 cm$^{-1}$ (400-200 nm). The absorption of UV radiation by a molecule leads to transitions among the electronic energy levels of the molecule.$^{31,32}$ The strength of UV spectroscopy lies in its ability to measure the extent of multiple bond or aromatic conjugation within molecules as illustrated in Figure 2.4.

Electrons in the vast majority of molecules fall into three classes: $\sigma$ electrons, $\pi$ electrons, and non-bonding electrons ($n$-electrons). In chemical terms, single bonds contain $\sigma$ electrons, multiple bonds $\pi$ electrons, and atoms to the right of carbon (e.g. O, N) contain $n$-electrons. The $\sigma$ electrons are the most tightly bound to the nuclei and hence require the most energy to undergo transitions, while the $\pi$ and $n$-electrons require less energy.

![Figure 2.4](image)

Figure 2.4 The regions of the electronic spectrum and the type of transition that occurs in each.
UV analysis was performed on the additive and the alkylphenol (one of the main starting components) in petroleum ether at sufficiently low dilution to obey the Beer-Lambert law. This empirical law governs the absorption of light by molecules. It is derived from two distinct laws: Beer's law relates the absorption to the concentration of the absorbing solute, and Lambert's law relates the total absorption to the optical path length, i.e.

\[
\log\left(\frac{I}{I_0}\right) = \varepsilon \cdot c \cdot l \quad \text{or} \quad \varepsilon = \frac{A}{c \cdot l}
\]

where, \(I_0\) is the intensity of the incident light, \(I\) is the light transmitted through the sample, \(\log (I_0/I)\) is the absorbance \((A)\), \(c\) is the concentration \((\text{mol dm}^{-3})\), \(l\) is the path length of the sample \((\text{cm})\) and \(\varepsilon\) is the molar absorption coefficient.

**Alkylphenol**

The structure of the alkylphenol is given in Figure 2.1. The concentrations are presented in Table 2.1, along with those of the additive. A graph of \(\log\) concentration vs. \(\log\) absorbance was plotted, which yielded a straight line with a slope of 1.048 demonstrating that the Beer-Lambert law is obeyed.

The spectrum of the alkylphenol (Figure 2.5(a)) shows two absorption maxima at 220 and 276 nm, which are quite close to the literature values for phenol, 210.5 and 270 nm. These are probably due to the \(\pi-\pi^*\) (so-called 'forbidden') transitions labelled \(E_1\) and \(B\), respectively. In benzene these appear at 204 and 256 nm but are shifted to higher wavelengths ('bathochromic shift') by virtue of hyper-conjugation with the alkyl and \(-\text{OH}\) substituents. In the case of the alkyl moiety this is caused by the overlap of the electrons of the alkyl \(C-H\) bond participating in resonance with the benzene ring.
or orbitals. Alkyl substitution moves the absorption to longer wavelengths. The bathochromic shift is progressive as the number of alkyl groups increases, and results from hyper conjugation in which the σ-electrons of the alkyl group are mobile enough to interact with the chromophoric group. The methyl group is more effective in hyper conjugation than other alkyl groups. Substitution of auxochromic groups (-OH, -NH$_2$) shifts the E- and B-bands to longer wavelengths, frequently with intensification of the B-band and loss of its fine structure because of n-π conjugation.

**Additive**

The UV spectrum of the additive (Figure 2.5(b)) again shows two absorption maxima at 220 and 313 nm, with the B-band shifted to a considerably higher wavelength. An unsubstituted phenate anion has E$_2$ and B bands at 235 and 287 nm respectively, which can be attributed to the non-bonding electrons in the anion interacting with the π electrons in the benzene ring. Conversion of the phenol to the phenate anion results in a bathochromic shift of the E$_2$ and B-bands and an increase in $\varepsilon_{\text{max}}$ because the non-bonding electrons in the anion are available for interaction in the π-electron system of the ring. This gives evidence that the phenate anion is present in the additive rather than the phenol. GAUSSIAN92 calculations on the phenol molecule and the unsubstituted phenate anion gave values of 192.5 (phenol) and 200.3 (phenate) nm for the E$_2$ band and 202.9 (phenol) and 247.4 (phenate) nm for the B band. Although the absolute positions of the peaks are up to 50 nm lower than the experimental values, the relative shifts on going from the phenol to the phenate are very similar. Therefore the *ab initio* calculations give some support for the existence of the phenate moiety in the additive.
Figure 2.5 UV spectra of (a) alkyl phenol and (b) 250 TBN additive
2.3.2 Fourier Transform Infra-red spectroscopy

Infra-red radiation is the part of the electromagnetic spectrum between the visible and microwave region (4000-625 cm\(^{-1}\)).\(^{34}\) Infra-red radiation is absorbed and converted by molecules into molecular vibration - this occurs as bands not lines, because a single vibrational energy change is accompanied by a number of rotational energy changes. Absorption of IR radiation can generally be assigned to specific functional groups that have characteristic vibrational frequencies. In contrast to the relatively few absorption peaks observed in the UV region for organic compounds, the infra-red provides a rich array of absorption bands, many of which cannot be assigned accurately. However, those that can be assigned can provide some useful information about the functional composition of the molecules.\(^{35}\)

The FTIR spectra of the alkylphenol, base oil and the additive were taken, shown in Figure 2.6.

**Base Oil**

The spectrum of normal paraffin is dominated by 4 vibrations, stretching and bending of C-H and C-C bonds. The C-C bending vibrations occur at very low frequencies (<500 cm\(^{-1}\)). The bands assigned to C-C stretching occur at 800-1200 cm\(^{-1}\). The most characteristic vibrations however are those arising from C-H stretching and bending. Absorption arising from the C-H stretching in the alkane occurs in the region 2840-3000 cm\(^{-1}\). The spectrum of the base oil has strong absorption bands at 2960 and 2830 cm\(^{-1}\), medium absorption bands at 1470 and 1390 cm\(^{-1}\), and a weak band at 725 cm\(^{-1}\). The spectrum of 'Nujol', which is a mixture of saturated hydrocarbons, contains absorptions resulting from vibrations typical of groups that are very similar to those found in the base oil, \textit{i.e.} C-H stretching at 2950 and 2820 cm\(^{-1}\), -CH\(_2\)- bending at
1458 cm\(^{-1}\), and C-CH\(_3\) bending at 1458 and 1380 cm\(^{-1}\). There is also a weak absorption at 722 cm\(^{-1}\) that is caused by bending vibrations of the group \(-(\text{CH}_2)_n\) where \(n\) is greater than 4.\(^{36}\) This gives evidence for the paraffinic nature of the base oil. The main features of the spectrum are given in Table 2.3.

**Alkylphenol**

The characteristic bands observed in the spectra of alcohols and phenols result from -OH and C-O stretching. The spectrum of the alkylphenol is shown in Figure 2.6. The band at 3330 cm\(^{-1}\) results from -OH stretching. The -OH bending frequency associated with phenols is observed at 1200-1300 cm\(^{-1}\). The band at 830 cm\(^{-1}\) is evidence of a 1,4-disubstituted benzene ring, which is the result of the bending of two adjacent aromatic C-H groups. The main features are summarised in Table 2.3.

GAUSSIAN92 calculations were performed on phenol, and gave two intense peaks at 3655 and 1234 cm\(^{-1}\) (which are absent in the corresponding benzene calculation). This strongly suggests that the peaks in the real spectrum (at 3330 and 1241 cm\(^{-1}\)) are from the -OH group. Although it is difficult to make quantitative comparisons between the model and experimental intensities, the intensities of the calculated peaks are roughly the same for the OH stretch and bend, just as for the experimentally measured phenol spectrum.

**Additive**

The main structural feature of the spectrum of the additive (Figure 2.6) which distinguishes it from that of the alkylphenol is the disappearance of the -OH stretching and bending peaks at 3339 and 1234 cm\(^{-1}\) and the appearance of a broad band centred at 1466 cm\(^{-1}\). The quantum mechanical calculations also produced a broad intense band, this time at 1489 cm\(^{-1}\). The intensity of this calculated band is roughly
six times that of the calculated -OH bands. The corresponding experimental peaks are also more intense (approximately four times the intensity of the experimental -OH peaks). This is further evidence that the phenate anion is in the additive. The peak at 862 cm⁻¹ (D in Figure 2.6) in the spectrum of the additive indicates the presence of carbonate. The spectrum of calcium carbonate was recorded and is annotated onto the figure in the area of interest. The literature value for carbonate is 854 cm⁻¹.³⁷ As with the alkylphenol, there is a band at 830 cm⁻¹ indicating the presence of two adjacent aromatic C-H groups. However, there is also a band at 880 cm⁻¹ which is characteristic of one aromatic C-H group. This provides support for the proposed structure shown in Figure 2.1. Another notable feature of this spectrum is the existence of a band at 1090 cm⁻¹, which could be from C-S stretching.

The GAUSSIAN92 code predicts aromatic C-H stretching frequencies at 3070-3080 cm⁻¹ for benzene, phenol and phenate, which compares favourably with the literature value of 3040 cm⁻¹. These are however obscured in the experimental spectra by the presence of the much stronger bands of saturated -CH₂ and -CH₃ groups from the alkyl chains.

Spectra of neat samples of each of the three synthesised samples (150, 250 and 300 TBN) were recorded, and are shown in Figure 2.7. As the TBN increases the bands at 1466 and 860 cm⁻¹ increase in intensity, which is in the order of relative carbonate content. Said and co-workers suggested that IR can be used to determine the base number of overbased sulphonates,³⁸ so it is possible that Infra-red spectroscopy could be used to determine TBN.
Table 2.3 Assignments of the FTIR spectra of the base oil, alkylphenol and additive. (The numbers in brackets are from GAUSSIAN92)

<table>
<thead>
<tr>
<th>Base Oil /cm⁻¹</th>
<th>Alkylphenol /cm⁻¹</th>
<th>Additive /cm⁻¹</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3339 (3655)</td>
<td>2954 2960 2957</td>
<td>O-H stretching</td>
</tr>
<tr>
<td>2954</td>
<td>2960 2930 2872</td>
<td></td>
<td>CH₃, C-H stretching</td>
</tr>
<tr>
<td>2924</td>
<td>2930 2872</td>
<td>2926 2871</td>
<td>CH₂, C-H stretching</td>
</tr>
<tr>
<td>2854</td>
<td>1612 1597 1552</td>
<td>1640</td>
<td>C-C ring stretch</td>
</tr>
<tr>
<td></td>
<td>1514 (1537, 1529)</td>
<td>1503</td>
<td>evidence for substituted</td>
</tr>
<tr>
<td></td>
<td>1463 (1454)</td>
<td></td>
<td>substituted benzene ring</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1466 (1489)</td>
<td>phenate intense band</td>
</tr>
<tr>
<td>1377</td>
<td>1379 1379</td>
<td>1379</td>
<td>CH₃, C-H bending</td>
</tr>
<tr>
<td></td>
<td>1241 (1234)</td>
<td></td>
<td>O-H bending</td>
</tr>
<tr>
<td></td>
<td>1181 (1181) 1114 (1119)</td>
<td>1180 (1143) 1078 (1081)</td>
<td>C-O bending</td>
</tr>
<tr>
<td></td>
<td>829 (805)</td>
<td></td>
<td>evidence for two adjacent</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>aromatic C-H</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>carbonate CO₃</td>
</tr>
<tr>
<td>722</td>
<td>728 728</td>
<td>728</td>
<td>CH₂ rocking</td>
</tr>
</tbody>
</table>
Figure 2.6 FTIR spectrum of the alkyl phenol (- - - -) and 250 TBN additive (—). A, OH stretching in alkyl phenol; B, evidence for phenate anion in additive; C, OH bending in alkyl phenol; D, evidence of carbonate in additive.
Figure 2.7 FTIR spectra of (a) 150 TBN phenate, (b) 250 TBN phenate and (c) 300 TBN phenate.
2.3.3 Nuclear magnetic resonance

Nuclear magnetic resonance spectroscopy (NMR) is concerned with the magnetic properties of certain atomic nuclei, notably the nucleus of the hydrogen atom (the proton) and that of the carbon-13 isotope of carbon. Studying a molecule by NMR enables differences in the magnetic properties of the various magnetic nuclei present to be recorded, and to deduce the chemical composition and some aspects of the structure of the molecules. The observed NMR frequencies are dependent on the molecular environment of the nucleus. The surrounding electrons shield the nucleus so that the effective magnetic field felt by the nucleus is not the same as the applied field. Electronic shielding arises from an induced circulation of electrons about a nucleus, which results in the generation of a field that opposes the applied field. Different environments are shielded to different extents, giving rise to a separation of the frequencies - this is termed the chemical shift, \( \delta \), and is usually measured with respect to a standard (usually trimethylsilane, TMS). The degree of shielding is dependent on the electron density around the proton. The higher the electron density the greater the shielding, i.e. lower \( \delta \) values.\(^{36}\)

\(^1\)H NMR measurements at 300 MHz of the alkylphenol, base oil and the additive diluted in deuterated chloroform were carried out using a Bruker NMR spectrometer. Proton resonance frequencies can be measured with an accuracy of \( \pm 0.02 \) ppm relative to an internal standard.

Solid-state \(^{13}\)C NMR was performed on the precipitated active component of the additive in the powdered form utilising a Bruker Solid-State NMR Spectrometer. There are difficulties in the application of NMR to the solid state, which are mainly due to very broad resonances normally occurring. These are caused by a number of factors, one of which is the phenomenon of dipolar broadening that results from local fields induced from other nuclei.\(^{35}\) In gas and liquid phases, dipolar broadening can be
ignored as the molecules tumble rapidly, isotropically and chaotically, at a sufficient rate that the NMR parameters are averaged to their isotropic values. In solids, motion is generally restricted and little averaging takes place. Spinning the sample rapidly about an axis making an angle, $\beta$ with the magnetic field $B_0$ as shown in Figure 2.8 is considered the equivalent of molecular tumbling in liquids. All the relevant anisotropic magnetic interactions have a leading energy term that depends on $(3\cos^2\theta - 1)$, where $\theta$ is the angle between a molecule-fixed axis and $B_0$. Spinning about the angle $\beta$ leads to an average function,

$$\langle 3\cos^2 \theta - 1 \rangle \propto \langle 3\cos^2 \beta - 1 \rangle$$

If $\beta$ is set at 54.7° all anisotropy effects are removed and each powder pattern reduces to a single line at a frequency governed by the relevant isotropic chemical shift. This technique is termed *Magic Angle Spinning*.39

![Diagram](image)

*(a)* arrangement for Magic Angle Spinning, *(b)* pulse sequence for $^1H$-$^13C$ Cross Polarisation. The duration of the 90° pulse is ~4μs, whereas the contact time (CT) is 2ms.

(DC=decouple)
Since the majority of solid samples contain protons, heteronuclear and homonuclear dipolar interactions cause further line broadening. This problem is rectified by employing a pulse sequence called 'Cross Polarisation' which is illustrated in Figure 2.8(b). Under the appropriate conditions magnetisation flows from protons to $^{13}$C during the contact time (CT), when resonant radio frequencies are applied to both protons and the nuclei being observed ($^{13}$C). The main advantage of solid-state NMR is that it is applicable to both crystalline and amorphous samples, because the chemical shifts are influenced only by the short-range environment of the relevant nucleus, whereas to take advantage of diffraction techniques requires long-range order. The technique seems very suitable for the overbased detergent systems because the cores are probably amorphous.

The individual spectra are discussed below.

**Base Oil**

The $^1$H NMR spectrum of the base oil is shown in Figure 2.9. Aliphatic protons are usually the most highly shielded of all common organic types, and would therefore be expected to exhibit chemical shifts at $\delta$ values of 0-2 ppm. The base oil shows chemical shifts of 0-2 ppm consistent with it being paraffinic in nature, although the range of chemical shifts observed indicates that the aliphatic chain is probably branched.

**Alkylphenol**

The 300 MHz $^1$H NMR spectrum of the alkylphenol dissolved in deuterated chloroform is shown in Figure 2.10 and gives a well-resolved spectrum. As expected
there are aliphatic protons at 0-2 ppm. The signal at 4.5 ppm is from the -OH groups, and those at 6-8 ppm aromatic in nature (Table 2.4).

**Table 2.4** Peak assignments for the $^1$H spectrum of alkylphenol.

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-2</td>
<td>Aliphatic protons</td>
</tr>
<tr>
<td>4-5</td>
<td>phenolic protons</td>
</tr>
<tr>
<td>6-8</td>
<td>aromatic protons</td>
</tr>
</tbody>
</table>

Integration of the signals gives a ratio which is consistent with there being 1 phenolic proton, 4 aromatic protons and 25 aliphatic protons, indicating a C$_{12}$ carbon chain. The integrals of the aliphatic proton peaks (0-2 ppm) suggest a branched rather than a linear chain as over 40% of the protons are from methyl protons.

As discussed previously, the alkyl phenol is made by alkylating phenol with propene tetramer which is branched. For steric reasons the alkyl chain is believed to substitute in the para-position, although the degree of branching is still unknown and the alkyl phenol is probably a mixture of several isomers. However, alkylation of the phenol occurs more readily at the para-position. The aromatic section of the spectrum clearly shows two different proton environments within the sample. This is inconsistent with purely para-substitution and gives evidence for some meta-substitution of the phenol.
Additive

The $^1$H spectrum of the additive in the base oil (Figure 2.11), in contrast to the spectrum of the alkylphenol, was poorly resolved, with only the aliphatic proton signals being clearly apparent. No aromatic protons are evident. To eliminate the signal of the base oil, the active component was extracted from the oil by the procedure described earlier. However, the re-dispersed adduct did not produce a noticeable aromatic signal either. The poor response in the aromatic region of the adduct, could be caused by the high charge on the metal ion, ($\text{Ca}^{2+}$), which renders the aromatic region immobile on the NMR time scale so that dipole-dipole interactions are not averaged to zero, thus resulting in a broad signal. However, $^{13}$C solid state NMR, utilising the technique of magic angle spinning was able to reveal both aliphatic protons at $\delta=9-43$ ppm and the aromatic part of the adduct, as well as the carbonate core, because the technique eliminates dipolar broadening. The NQSTOSS pulse sequence eliminates non-quaternary carbons (i.e. those that have protons directly attached). The $^{13}$C solid state NMR spectrum of the adduct is shown in Figure 2.12. The carbonate peak occurs at $\delta=168$ ppm, and there are two other well-defined peaks centred on $\delta=120$ and 136 ppm, indicating that there are at least two different aromatic carbon environments, which could be from the ortho-C-S bridge and C-O groups, respectively. It should be noted that this is the only technique that has probed the carbonate core region of the molecule. However the peaks are very broad indicating a disordered core, which is in agreement with EXAFS studies on similar sulphonate systems.$^{19}$ Subsequent dissolution and re-extraction of the sample did not improve the quality of the signal.

The $^{13}$C solid-state NMR spectra were performed using a Bruker NSL 300 MHz machine operating at a frequency of approximately 75MHz.
Figure 2.9 $^1$H NMR spectrum of base oil.

Figure 2.10 $^1$H NMR spectrum of alkyl phenol.
Figure 2.11 $^1$H NMR spectrum of 250 TBN additive.

Figure 2.12 $^{13}$C solid state NMR of 250 TBN adduct.
2.4 Thin Layer Chromatography

Thin layer chromatography (TLC) is used for the separation of a wide variety of substances in which one phase is stationary and one is mobile. The sample components are applied to the stationary phase and are gradually separated into discrete bands as the mobile phase moves along the plate as a result of capillary action. At the end of the process, the components are separated in order of increasing attraction with the stationary phase, i.e. the least retarded component emerges first and the most strongly retained component emerges last. The whole process is summarised in Figure 2.13.

![Diagram of Thin Layer Chromatography Process]

**Figure 2.13** The process of Thin Layer Chromatography
2.4.1 Experimental

A range of concentrations (1-10% by weight) of the adduct in toluene were prepared.

I. 1, 2 or 3 µl of sample in toluene was applied to a silica gel TLC plate, which was then dried in an oven for 2 minutes.

II. The plate was developed in a tank by allowing a 4:1 mixture of toluene:methanol to rise up the plate a set distance. The plate was then removed, the solvent allowed to evaporate in a fume cupboard and the plate then dried in an oven.

III. The plate was then scanned at 280 nm under a UV lamp to enable visual inspection of any separation, which was also quantified automatically using a densitometer.

Interpretation of the TLC plate

A typical TLC plate is shown diagramatically in Figure 2.14. The value 'a' is the distance moved by the solvent, and 'b' is the distance (to the centre of the spot) moved by the compound.
Compounds can be characterised by their $R_f$ values where $R_f$ is the 'retention factor'. $R_f$ values vary between 0 and 1, and is a constant for a particular compound under identical conditions (temperature, type of plate, solvent). The higher the $R_f$ value the less affinity for the stationary phase relative to that of the solvent.

### 2.4.3 Results

The neat detergent additive was run along with the extract and two of the starting components i.e. alkylphenol and base oil. The chromatograms are shown in Figure 2.15. The $R_f$ values are given for each compound in Tables 2.5-2.8.

Figure 2.15(a) shows the chromatogram of the base oil, which has two characteristic peaks at 52 and 122 mm respectively. The chromatogram of the alkylphenol (Figure 2.15(b)) shows five peaks at 53, 74, 88, 102 and 124 mm, the peaks at 53 and 124 being attributed to the base oil in the sample. The $R_f$ values for these samples are given in Tables 2.5 and 2.6.
Table 2.5  \( R_f \) values for the base oil

<table>
<thead>
<tr>
<th>peak</th>
<th>distance moved (mm)</th>
<th>( R_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39.98</td>
<td>0.280</td>
</tr>
<tr>
<td>2</td>
<td>110.03</td>
<td>0.770</td>
</tr>
</tbody>
</table>

Table 2.6  \( R_f \) values for alkylphenol

<table>
<thead>
<tr>
<th>peak</th>
<th>distance moved (mm)</th>
<th>( R_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41.46</td>
<td>0.290</td>
</tr>
<tr>
<td>2</td>
<td>62.10</td>
<td>0.434</td>
</tr>
<tr>
<td>3</td>
<td>76.48</td>
<td>0.535</td>
</tr>
<tr>
<td>4</td>
<td>89.75</td>
<td>0.628</td>
</tr>
<tr>
<td>5</td>
<td>111.87</td>
<td>0.783</td>
</tr>
</tbody>
</table>

The neat additive was investigated as well as the adduct powder and each was dissolved in toluene. The TLC chromatogram is given in Figure 2.15(c). As can be seen there are seven peaks at 42, 49, 51, 53, 74, 80 and 123 mm. The peaks at 53 and 123 mm are evidence of the base oil in the compound while the peak at 74 mm is from residual unreacted alkylphenol in the additive. The spectrum of the adduct (Figure 2.15(d)) shows no base oil peaks and no evidence for residual alkylphenol.

This technique has proved that the isolation procedure (acetone precipitation) has indeed only removed any unwanted residual compounds. The TLC method proves to be a very useful method for providing information on the chemical components in these systems. Up to now it has been little used for these compounds.
### Table 2.7 - \( R_f \) values for neat additive

<table>
<thead>
<tr>
<th>peak</th>
<th>distance moved (mm)</th>
<th>( R_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30.03</td>
<td>0.210</td>
</tr>
<tr>
<td>2</td>
<td>36.66</td>
<td>0.257</td>
</tr>
<tr>
<td>3</td>
<td>38.88</td>
<td>0.272</td>
</tr>
<tr>
<td>4</td>
<td>42.56</td>
<td>0.298</td>
</tr>
<tr>
<td>5</td>
<td>61.73</td>
<td>0.432</td>
</tr>
<tr>
<td>6</td>
<td>67.63</td>
<td>0.473</td>
</tr>
<tr>
<td>8</td>
<td>109.66</td>
<td>0.767</td>
</tr>
</tbody>
</table>

### Table 2.8 - \( R_f \) values for the adduct

<table>
<thead>
<tr>
<th>peak</th>
<th>distance moved</th>
<th>( R_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>38.88</td>
<td>0.272</td>
</tr>
<tr>
<td>2</td>
<td>41.08</td>
<td>0.288</td>
</tr>
<tr>
<td>3</td>
<td>43.67</td>
<td>0.306</td>
</tr>
<tr>
<td>4</td>
<td>67.26</td>
<td>0.471</td>
</tr>
<tr>
<td>5</td>
<td>83.16</td>
<td>0.582</td>
</tr>
</tbody>
</table>
Figure 2.15 TLC chromatograms; (a) base oil, (b) alkyl phenol, (c) 250 TBN neat additive and (d) 250 TBN adduct.
2.5 Summary

This chapter has provided evidence for the existence of the calcium phenate and calcium carbonate as the two predominant chemical species in the additive. The synthesis procedure is very effective at going to the desired products with negligible unreacted starting chemicals in the final product. There is no evidence of any other species e.g. Ca(OH)$_2$ or CaO. TLC showed that the isolation procedure removes all the base oil and any unreacted alkylphenol.

Therefore the work reported in this chapter has identified the chemical species in these products but has not been concerned with the physical nature of the detergent particles, which is covered in the next chapter.
Chapter 3. Interfacial Characterisation
3.1 Introduction

The detergent systems that are the subject of this thesis are believed to be colloidal in nature as discussed previously. Surface science experiments were carried out to characterise these systems. The results of these studies are reported in this chapter. The size of the particles and the interactions between them have been determined.

Particles in colloidal dispersions are essentially two-phase systems. The interface between dispersed phase and the dispersion medium plays an important role in determining the stability and properties of the whole system. The molecules of surface active materials have a strong affinity for interfaces because they contain both hydrophilic and lipophilic (oil-loving) regions. The surface tension of the overbased detergent systems was measured and used to determine the interfacial characteristics of the particles.

The size and shape of colloidal particles determine many features of the behaviour of the colloidal suspension. There are numerous methods for particle size determination including, Small Angle Neutron Scattering (SANS), Small Angle X-ray Scattering (SAXS), Light Scattering and Langmuir Trough measurements. The overbased detergent systems are insoluble in water, but soluble in a wide range of non-aqueous solvents (e.g. hexane, toluene etc.) and this property can be used to determine the size of the active particles in the additive using the Langmuir trough technique, which is described in this chapter.
3.2 Determination of Density

As the surface properties of these detergents were determined in a number of different solvents, it was essential to determine the density of each adduct. The active species was isolated from the additive using the method described in chapter 2. The density of each powdered adduct was determined using the density bottle method, which is described below.

1. A 10 ml density bottle was thoroughly cleaned and weighed.
2. The density bottle was filled with a solvent of known density (toluene, \( \rho = 0.867 \text{ g cm}^{-3} \)) and weighed. The volume of the density bottle was then determined.
3. The bottle was cleaned, dried and a reasonable amount of the powdered adduct added. The bottle was weighed again.
4. Toluene was added to the bottle until it was half full (ensuring all the powder dissolves). Then the bottle was filled with the toluene and the weight recorded.
5. The volume occupied by the particles was subsequently found and the density determined.

<table>
<thead>
<tr>
<th>TBN</th>
<th>Density (g cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>1.018</td>
</tr>
<tr>
<td>250</td>
<td>1.228</td>
</tr>
<tr>
<td>300</td>
<td>1.329</td>
</tr>
</tbody>
</table>
3.3 Langmuir Trough Studies

Many insoluble substances can be spread on to a water surface, and will form a surface film one molecule thick. These monolayers represent an extreme case in adsorption at liquid surfaces, as all the molecules are concentrated in one molecular layer at the interface. Because these overbased surfactants have a negligible solubility in water, insoluble monolayers cannot be conveniently formed by adsorption from bulk solution but they have to be formed from a spreading process at the interface.

Much can be learned about the size and shape of the individual molecules by studying the physical properties of the monolayer. The particle size and the interaction potential between them can be determined using the Langmuir Trough method, the theory of which was extended to hydrophobic particles by Clint and Taylor.43

The first apparatus for studying the relationship between surface tension and film area was developed by Agnes Pockels in 1891. This consisted of a shallow trough with moveable tin barriers which confined an insoluble monolayer to a known area. A modern commercial version of this basic design is the Lauda FW2 Langmuir Filmwaage trough, which was used for these studies. This apparatus has the ability to determine directly the surface pressure by measuring the horizontal force exerted on a floating boom whose length is just less than the internal width of the trough. A small amount of sample in a suitable spreading solvent is applied to the surface to form a monolayer which is confined on a known area of the water surface by a hydrophobic barrier. The horizontal force acting on a boom of length l is equal to II, where II is the surface pressure. This is equal to the difference in surface tension between the clean water behind the boom and the monolayer coated water in front. A schematic representation of the trough is given in Figure 3.1. The force is measured using a sensitive force transducer. Since this technique is very sensitive to contaminants, the
water subphase was purified using a Milli-Q purifier and cleaned several times to ensure a clean water surface. This is very important as there are very few active molecules present in the monolayer. This technique has traditionally been the used for long chain polar molecules (e.g. fatty acids). In 1969 Sheppard extended the use of the technique to obtain particle sizes for emulsion latexes from the pressure-area isotherms. The use of the technique was further extended to investigate much smaller colloidal particles by Clint and Taylor in 1991. They obtained particles sizes, interaction potentials and contact angles for a range of overbased detergents.

![Schematic diagram of the Langmuir trough](image)

**Figure 3.1 - Schematic diagram of the Langmuir trough**

The active species was extracted from the oils using the method described in chapter 2. The powdered adducts were made up as 0.5% w/w solutions in AR grade toluene (the spreading solvent). A small amount of sample (2×10⁻⁵ dm³) was then applied to the water surface (at 25 °C), and the apparatus left for several minutes to ensure that all the solvent had evaporated. The barrier was then swept across the surface and the change in surface pressure, Π, with surface area, A, was recorded.
3.2.1 Determination of Particle size.

As can be seen from the $\Pi$-A curve (Figure 3.2) there is a 'knee' which corresponds to the transition from a loosely packed solid-like arrangement of particles to a close-packed solid-like arrangement, as the area decreases.

![Figure 3.2 - Typical $\Pi$-A curve](image)

The 'knee' corresponds to the critical surface pressure $\Pi_c$, where there is a strong overlap between the stabilising shells and the particles form a two-dimensional layer in the surface plane. Further compression beyond this point could result in the formation of multilayers due to particle ejection from the interface. At even smaller surface areas, there is a further change in slope (shown in the diagram) which can be interpreted in terms of the formation of a more complete three-dimensional solid-like arrangement of the particles. The area at the knee is determined by drawing tangents at the inflexion.
points on either side of the knee and determining the intersection point. This is the close-packed area \textit{(i.e. when the surfaces of the particles are arranged in close proximity)}. If the particles are assumed to be monodisperse and spherical then they would form a hexagonally close-packed monolayer and the effective diameter, $\sigma$, can be calculated. However the effective volume per particle is equal to that of the circumscribing hexagon, which is derived in Figure 3.3 below,

\begin{center}
\includegraphics[width=0.5\textwidth]{hexagon.png}
\end{center}

\begin{itemize}
\item Area of the shaded triangle = \( \frac{1}{2} R \cdot \frac{R}{\sqrt{3}} = \frac{R^2}{2\sqrt{3}} \)
\item Area of hexagon (a) = \( 12 \cdot \frac{R^2}{2\sqrt{3}} = 2\sqrt{3}R^2 \)
\item Hexagon layer volume (b), \( V_{\text{eff}} = 2\sqrt{3}R^2 \times 2R = 4\sqrt{3}R^3 \)
\item and the actual sphere volume, \( V_{\text{act}} = \frac{4}{3} \pi R^3 \)
\item Correction factor = \( \frac{4\sqrt{3}R^3}{4 / 3 \pi R^3} = 1.654 \)
\end{itemize}

\textbf{Figure 3.3} Derivation of the correction factor

Assuming monolayer coverage, the diameter, $\sigma$, can be calculated from a knowledge of the amount of additive deposited on the surface, using the following formula,
where $\rho_S$ is the density of the solvent, $\rho_p$ is the bulk density of the powder particles, $\omega$ is the % weight concentration of the powder in toluene, $v$ is the volume of the solution deposited on the surface of the water, and $A_H$ is the area at close packing. Table 3.2 contains the relevant parameters along with results for each of the three samples investigated.

Table 3.2 Experimentally determined parameters for the different TBNs

<table>
<thead>
<tr>
<th>Property</th>
<th>150 TBN</th>
<th>250 TBN</th>
<th>300 TBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_s$ /g cm$^{-3}$</td>
<td>0.867</td>
<td>0.867</td>
<td>0.867</td>
</tr>
<tr>
<td>$\rho_n$ /g cm$^{-3}$</td>
<td>1.018</td>
<td>1.228</td>
<td>1.329</td>
</tr>
<tr>
<td>$v$ /ml</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>$\omega$ /%wt</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$\Pi_c$ /mNm$^{-1}$</td>
<td>22.97</td>
<td>26.25</td>
<td>28.0</td>
</tr>
<tr>
<td>$A_H$ /m$^2$mg$^{-1}$</td>
<td>0.629</td>
<td>0.570</td>
<td>0.503</td>
</tr>
<tr>
<td>$\sigma$ $^{(\pm0.05nm)}$</td>
<td>2.488</td>
<td>2.948</td>
<td>3.146</td>
</tr>
<tr>
<td>$\theta_c$ $^{(\pm0.03^{\circ})}$</td>
<td>114.01</td>
<td>111.47</td>
<td>110.19</td>
</tr>
</tbody>
</table>

Particle diameters of 2.49, 2.95 and 3.15 nm were calculated by this method for the 150, 250 and 300 TBN compounds respectively. This is consistent with previous overbased particle size determinations, for example, sulphonates have typical sizes in the region 2-5 nm$^{45}$ There is a linear relationship between TBN and particle diameter, as shown in Figure 3.4.
An extrapolation to zero TBN gives an estimate of the shell diameter of 1.90 nm, and therefore by subtraction the carbonate core diameters are 0.59, 1.05 and 1.25 nm respectively (neutron scattering of similar phenates has given a shell thickness of 1.5 nm). Figure 3.5 shows the relative sizes of the adduct particles drawn to scale.

![Figure 3.5](image)

Figure 3.5 Relative sizes of the adduct particles drawn to scale: (a) 150 TBN, (b) 250 TBN and (c) 300 TBN adduct.

Knowing the molar volume of CaCO₃ to be $3.6934 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$, we can estimate the number of CaCO₃ molecules in each compound using the following reasoning,

The volume per molecule, $V_m = \frac{\text{Molar volume}}{N_A}$

Volume of the core, $V_c = \frac{4}{3} \pi R^3$

therefore the number of CaCO₃ molecules $= \frac{V_c}{V_m}$

The number of phenate molecules can then be estimated by using the ratios determined in chapter 2 from quantitative analysis. The results for each of the compounds are given in Table 3.3.
Chapter Three: Interfacial Characterisation

Table 3.3 Numbers of CaCO$_3$ and CaPhe

<table>
<thead>
<tr>
<th>TBN</th>
<th>No. of CaCO$_3$ molecules</th>
<th>No. of CaPhe molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>250</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>300</td>
<td>16</td>
<td>8</td>
</tr>
</tbody>
</table>

Having established the core and shell diameters of the particles this enabled the determination of the available area per phenate, $A_p$, on the particle surface. For a given radius, $r$, from the centre of the particle, $A_p = 4\pi r^2/n_p$, where $n_p$ is the number of phenate molecules in the particle. Using the radii of the particle cores, $r = r_c$, we calculate there to be 0.54, 0.58 and 0.61 nm$^2$ surface area available to each phenate (for the 150, 250 and 300 TBN respectively) in the region of the head group. (The surface area of a molecule in a 400 TBN sulphonate shell in the region of the head group was found to be 0.4 nm$^2$). The total area available per phenate molecule using the maximum radius of each particle (core plus shell), is 9.72, 4.56 and 3.90 nm$^2$ for the 150, 250 and 300 TBN respectively. Clearly the amount of space depends markedly on where the hypothetical surface shell is positioned. Based on the core radius, the available area per phenate increases slightly with TBN. However, based on the outer radius of the particle, the reverse is the case. The most significant radius for stabilisation purposes probably lies somewhere in between these two extremes. As the solvent probes the outer region of the particle, it is probable that the latter outer limit is the most relevant for particle stabilisation. Using the latter limit, the lower TBN particles have a more open stabilising shell which allows more gross deformation of the whole phenate molecule under compression. The more crowded state of the phenate molecules in the highest TBN is probably the most influential factor in determining the upper limit on the maximum TBN that can be synthesised.
This is only relevant however if the particles are spherical. If they are cylindrical or disc-shaped the surface area per phenate is given by $2\pi ra$, where $a$ is the thickness of the cylinder or disc. Therefore the area available to each phenate will be less, but the same trend would result i.e. the lower TBN compounds would have more available area than the higher TBN compounds. The simulation work has provided evidence that these types of micelles are not spherical but disc shaped, and this is discussed in chapter four.
Figure 3.4 Dependence of particle size on TBN
3.3.2 Interaction Potential between particles

The kinematic viscosities measured for the additives can be used to estimate their effective volume fractions, $V_f$, using the Krieger-Dougherty expression for the relative (Newtonian) viscosity,

$$\eta_{r0} = \eta_0 / \eta_s$$

where $\eta_0$ is the Newtonian viscosity of the additive and $\eta_s$ is the viscosity of the base oil suspending medium,

$$\eta_{r0} = (1 - V_f / 0.63)^{-2}$$

eqn. 3-4

The viscosity diverges to infinity at a volume fraction equal to that of random close packing for spheres (0.63). Assuming the additive particles are spheres, this leads to effective solids volume fractions of 0.450, 0.538 and 0.563 for the 150, 250 and 300 TBN additives respectively. An independent measure of volume fraction can be obtained from the volume of the particles, $V_A$, (from its density and mass) and the volume of the oil $V_O$ (assumed constant throughout the synthesis) These data give $V_f = (V_A - V_O) / V_A$ of 0.505, 0.550 and 0.552 respectively. All the neat additives therefore contain highly close packed particles which would be in the fluid-solid two phase region of the hard sphere system (for comparison, the maximum fluid volume fraction of a hard sphere fluid is 0.49 and the volume fraction of the hard sphere crystal at melting is 0.54). Best agreement between the two methods for obtaining $V_f$ is for the 300 TBN. This indicates that the 300 TBN adduct particle is more closely like a hard sphere in its mutual interactions than the lower TBN adducts. Conventional colloid science theory based on stabilising layers would support this conclusion. For submicron particles (ca. 0.1 μm diameter) it is usually assumed that the shells are softer and more compressible than the cores. For a shell/core diameter ratio, $\kappa = \sigma_s / \sigma_c$, where $\sigma_s$ is twice the thickness of the phenate shell , and $\sigma_c$ is the carbonate core diameter, then the total volume fraction, $V_f = V_{fc}(1 + \kappa)^3$, where $V_{fc}$ is the volume fraction of the core. Using this formulation, the concept of an effective hard-sphere diameter
becomes less reasonable as TBN diminishes because $\kappa$ increases. The values of $\kappa$ for the 150, 250 and 300 TBN additives are 3.23, 1.81, 1.53 respectively. These are quite large in comparison to sterically stabilised sub micron colloidal particles, where values of $\kappa=0.5$ are considered large. Using this reasoning, the 300 TBN adduct particle should be more like a hard sphere than either the 150 or 250 TBN particles.

These particles are at least an order of magnitude smaller than typical colloidal particles to which this treatment is normally applied and therefore it is probable that the discrete atomistic nature and the rigidity of the alkyl chains is a more important factor in determining the interaction forces between the particles.

The interaction potential between the detergent particles can be obtained using the Langmuir trough data, from the $\Pi$-A data in the compression region up to the point of hexagonal close-packing. If it is assumed that the particles are still hexagonally close-packed, and occupy an area $A$, but are uniformly further apart, then the nearest neighbour separation, $s$, is given by,

$$\frac{s}{\sigma} = \left( \frac{A}{A_{\text{H}}} \right)^{1/2} \quad \text{eqn. 3-5}$$

The force between neighbouring particles can therefore be calculated. The surface pressure, $\Pi$, viewed microscopically, is the normal force per unit length of the barrier,$$
\Pi = \frac{F_n(r)}{\sigma} \quad \text{eqn. 3-6}
$$

From the hexagonal geometry, $F_n(r)=\sqrt{3}F(r)$, where $F(r)$ is the force between the two particles in the monolayer separated by a distance $r$. By plotting $F(r)/a$, where a is
the radius of each TBN, against \( r \), the interaction potential can be obtained. These are shown in Figure 3.6 for the three TBN systems.

The range of the separations in this region is approximately 10% of the core diameter, so that the assumption that the monolayer structure is still hexagonal below the close packed limit at the knee is reasonable.

A simple potential form which fits reasonably well to this data is the 'inverse-power' potential,

\[
\phi(r) = \varepsilon \left( \frac{\sigma}{r} \right)^n 
\]

where \( \varepsilon \) and \( \sigma \) are the characteristic energy and distance respectively.

The force \( F(r) = -d\phi(r)/dr \) between the particles is from the analytic form given in equation 3-7,

\[
F(r) = n \varepsilon \sigma^n r^{-(n+1)}
\]

A \( ln-ln \) plot of \( F(r) \) vs. \( r \) (Figure 3.7) showed that the 300 TBN adheres particularly well to the analytic form of equation 3-8 until the particles are very close, with a value of \( n = 20 \) (±6) obtained from the slope of the graph for all the TBNs. The region of the potential probed by the experiment for the 150 TBN is 2.49-2.71 nm, 2.96-3.27 nm for the 250 TBN and 3.21-3.48 nm for the 300 TBN. Therefore the chains are squashed by ca. 0.3 nm in each case up to close packing (the lower of the two values and used to determine \( \sigma \)). The chains are only receding by approximately 15% in each case, suggesting a branched chain structure rather than a linear chain structure which would be expected to contract to a greater extent.
From the $\sigma$ values of 2.49, 2.95 and 3.15 nm for the 150, 250 and 300 TBN adducts, values for the characteristic interaction energy can be obtained from the force curves. These give $\varepsilon/k_B T$ of 38, 70 and 93 respectively. A plot of $F/(n\varepsilon/\sigma)$ vs. $r/\sigma$ in Figure 3.8, gives a more quantitative assessment of the extent to which the potentials for the three additives follow the same generic analytical form, when scaled by the characteristic energy, $\varepsilon$, and distance, $\sigma$, which is seen to be reasonably good. Both $F/(n\varepsilon/\sigma)$ and $r/\sigma$ are dimensionless quantities and if the assumed force law applies to all of the TBN particles, the plots would be expected to be dependent on TBN. All these adduct particles have a similar 'hardness', which is presumably dominated by the rigidity of the phenate chains at the bond/atomic level. So far the Langmuir trough data has been used to calculate the forces between the adduct particles. The $\Pi$ vs. $A$ data can also be used to establish the relative hydrophobicities of these particles. More information on the nature of these detergent particles can be obtained by measurement of the contact angle, which is described in the next section.
Figure 3.6 - Force between neighbouring particles (normalised by the particle radius $a$) as a function of the separation of the particle centres, $r$. 
Figure 3.7 - A ln-ln plot of the force between the particles $F(r)$ versus the separation between the particle centres, $r$. 
Figure 3.8 - $F/(ne/\sigma)$ vs. $t/\sigma$. 

150 TBN
250 TBN
300 TBN
3.2.3 Contact Angle

The nature of the interaction between the particle and the solvent can be inferred from further analysis of the Langmuir trough data. In particular the degree of hydrophobicity of the particles can be estimated using the approximation that the surface pressure at the knee $\Pi_C$ of the $\Pi$ vs. $A$ curve is equal to the free energy change per unit area associated with the deposition of the particles on the water surface at close packing. This can be rationalised as follows. The area of contact between the particle and water is given by $2\pi R^2(1+\cos\theta)$, where $\theta$ is the contact angle (see Figure 3.9), and the flat area of the water surface missing as a result of the particle is $\pi R^2 \sin^2 \theta = \pi R^2 (1-\cos^2 \theta)$.

The free energy required to remove the particle from the water surface into the air is,

$$E = 2\pi R^2 (1+\cos \theta)(\gamma_{SA} - \gamma_{SL}) + \pi R^2 (1-\cos^2 \theta)\gamma_{LA}$$  eqn. 3-9

where $\gamma_{SA}$, $\gamma_{SL}$ and $\gamma_{LA}$ are the surface tension values between solid-air, solid-liquid and liquid-air respectively.

Using Young's equation,$^52$

$$\gamma_{SA} - \gamma_{SL} = \gamma_{LA} \cos \theta$$  eqn. 3-10

then eqn. 3-9 becomes,

$$E = \pi R^2 \gamma_{LA} (1 + \cos \theta)^2$$  eqn. 3-11

The number of particles per unit area at hexagonal close packing is,

$$N = 1 / \left[ 2\sqrt{3} R^2 \right]$$  eqn. 3-12
so that the free energy per unit area to remove the particles from the interface into the air becomes,

\[ \Delta G = EN = \pi y_{LA} (1 + \cos \theta)^2 / 2\sqrt{3} \]  

which is equal to the surface pressure at the point of hexagonal close packing (knee)

To remove the particles from the interface into the water, the same expression is used but containing a \((1-\cos\theta)^2\) term. The latter can be expressed in terms of the contact angle, \(\theta\), that the particles make with the water surface. This is illustrated in Figure 3.9,

\[ \Pi = \frac{\pi y_{LA}[1 \pm \cos \theta]^2}{2.3^{1/2}} \]  

where, \(y_{LA}\) is the air/water surface tension = 72 mN m\(^{-1}\).
For a given critical surface pressure, this gives a sharply peaked $\Pi_c(\theta)$ function, with a maximum at $90^\circ$, which is shown in Figure 3.10. ($90^\circ$ is equivalent to the maximum in pressure required to expel the particle from the surface). It should be noted that there are two angles for each compound, the higher ones reflecting the fact that the particles are more easily pushed into the air, and it is these values that are discussed here. (The converse is true for the lower angles). The critical pressures are 23.0, 26.3 and 28.0 mNm$^{-1}$ for the 150, 250 and 300 TBN adducts, respectively. Contact angles calculated from these values of $\Pi_c$ for the three TBNs are 114.0, 111.5 and 110 ($\pm0.5$) $^\circ$ respectively. The larger the contact angles, the more hydrophobic are the particles. This indicates that the lower TBNs are slightly more hydrophobic, which is reasonable as they have relatively less carbonate in the core when compared with the hydrophobic surfactant component.

The angles are roughly proportional to $\Pi_c$ on this part of the $\Pi_c(\theta)$ curve. Despite the presumed improvement in the hydrophobic screening of the shells with increasing TBN, the lower TBNs appear to be more hydrophobic in the water interface region. In the lower TBN particles, the ratio of surfactant/carbonate is greater than for the higher TBN particles which explains this trend. To investigate further these interfacial trends, surface tension measurements were performed, the results of which are described in section 3.3.

![Figure 3.10](image.png)

Figure 3.10 Surface pressure vs. contact angle curve.
3.4 Surface Tension Measurements

In order to expand the area of an interface \textit{i.e.} to bring molecules from the interior to the surface, work must be done against the cohesive forces in the liquid. It is well known that short-range forces of attraction exist between molecules, and are in fact responsible for the liquid state. The molecules which are located in the bulk are subjected to equal forces of attraction in all directions, whereas those at the surface experience unbalanced forces of attraction resulting in a net inward pull. Figure 3.11 illustrates this for molecules at the air-water interface.\textsuperscript{53}

![Figure 3.11 Attractive forces between molecules at the surface and in the interior of a liquid.](image)

It follows that the surface portions of the liquid have a higher free energy than the bulk liquid, which gives rise to a 'surface tension' acting parallel to the surface which opposes any attempt to extend the interface. A tension is a negative pressure; pressure is the force per unit length in two dimensions, so that the surface pressure has units of force per unit length. If the surface tension is $\gamma$, then the work performed on the surface in extending its area by an amount $dA$ is,
\[ dW = ydA = dG \]
\[ dG = ydA \]

where \( dG \) is the free energy change.

A surfactant (e.g. a detergent molecule) is a species that is present (or 'active') at the interface between two phases. Detergent molecules accumulate at the interface between hydrophilic and hydrophobic phases and reduce the surface tension. The strong adsorption of such materials at interfaces is termed \textit{surface activity}. The extent of adsorption at a liquid surface can be estimated from the effect of solute concentration on surface tension data using the Gibbs adsorption equation,\(^{54}\)

\[ d\gamma = -\sum_i \Gamma_i d\mu_i, \]

\text{eqn. 3-15} 

where \( \Gamma_i \) and \( \mu_i \) are the surface excess concentration and chemical potentials respectively of species \( i \). This equation can be simplified by assuming that the two phases (oil and water) are separated by a geometrically flat surface, i.e. only the detergent accumulates at the interface and the boundary between the solvents is positioned so that \( \Gamma = 0 \) for the solvent systems. The Gibbs equation then becomes,

\[ d\gamma = -\Gamma_D d\mu_D \]

\text{eqn. 3-16} 

for the detergent (D) molecules.

For dilute solutions, \( d\mu_D = RTd \ln C_D \), where \( C_D \) is the concentration of detergent in the bulk liquid. Therefore,

\[ d\gamma = -(RT / C_D) \Gamma_D dC_D \]

\text{eqn. 3-17} 

at constant temperature.
If the detergent accumulates at the interface, its surface excess concentration is positive and so $(\partial \gamma / \partial C_D)$ is negative i.e. the surface tension decreases with increasing bulk solute concentration. The relative surface tensions for the adducts dissolved in hydrophobic solvents will therefore order them in a hydrophobicity scale.

### 3.4.1 Experimental Apparatus

Surface tension measurements were performed using a Kruss Digital Tensiometer K10. The active species were isolated from the oils as described in chapter 2, and the adducts prepared as 1, 5 and 10 % by weight solutions in toluene. Higher concentrations were attempted but these were too viscous to give reasonable results. The measurements were taken using the DuNouy ring method, which is illustrated in Figure 3.12. In this method the measuring body is a horizontally suspended wire ring of radius, $R$, which is immersed into the solution and then withdrawn from the interface to the point where the neck of the liquid hanging below it breaks away. As the ring is raised, in addition to the hydrostatic weight of the liquid underneath, there is a resultant force of surface tension acting along the wetting line. This resultant force is equal to the length of wire in contact with the ring multiplied by the force per unit length, i.e., $F = 4\pi R \gamma$, where $\gamma$ is the liquid-air surface tension. Therefore measurement of the 'breaking' force leads directly to a value for the surface tension.

![Figure 3.12 DuNouy Ring apparatus](image)
3.4.2 Surface Tension Results

A graph of surface tension vs. log concentration is plotted in Figure 3.13. (The surface tension of toluene is 28.7 mNm). The concentrations are given as molarities, assuming an RMM of 1374, 4523 and 6297 for 150, 250 and 300 TBN adduct particles based on the total number of molecules in the particle. It can be seen that for each compound, the surface tension decreases with increasing bulk concentration indicating a positive adsorption at the interface in accord with the Gibbs adsorption isotherm. The more negative the slope of the surface tension with respect to bulk particle concentration, the more positively adsorbed at the interface are the adduct particles, and therefore the less hydrophobic they are. It can be seen that the slopes for the 250 and 300 TBN adducts are greater than that of the 150 TBN adduct. This indicates that the 150 TBN adduct is more hydrophobic than the other two, and is therefore more chemically similar to the solvent (toluene). This is consistent with the Langmuir trough results. The 250 and 300 TBN adducts would appear to be less compatible with the solvent and diffuse to the surface. However the surface tension results are indicating that the 250 TBN molecule is less hydrophobic than the 300 TBN compound as it is more positively adsorbed at the interface, which is in disagreement with the trend obtained form the Langmuir trough work. This difference could arise from the fact that the two experiments were performed using quite different solvents, i.e. water in the Langmuir trough experiments, as opposed to toluene for the surface tension measurements. Therefore it is possible that the states of the particles could be different in the two solvents, which would give rise to the different order in the apparent hydrophobicities. The Langmuir trough experiments were performed on a water surface, and it is likely that the surfactant chains of the additives are in a collapsed state, whereas in the toluene (surface tension) the chains are probably more extended into the solvent, facilitating favourable interactions between the toluene and the aryl moieties in the phenate.
The fact that the 300 TBN compound has a greater affinity for the toluene than the 250 TBN compound is indicating that the structure of the two is quite different. In fact, computer simulation studies (chapter 4) have shown that this is indeed the case. The 250 TBN micelle is disc shaped with exposed carbonate at either side. The 300 TBN, which has a greater number of surfactant molecules than the 250 TBN, is more 'ellipsoidal' with the surfactant chains protecting/covering the exposed parts of the carbonate core. In water the surfactant chains are likely to retract more, and therefore play a relatively smaller role than the carbonate core. Hence on water, the particles are more hydrophobic in the order 150 through to 300 TBN in line with the relative increase in carbonate content.
Figure 3.12 Surface tension vs. ln concentration of detergent.
Chapter Three: Interfacial Characterisation

3.5 Summary

The work reported in this chapter has provided information on the physical nature of these phenate detergent particles. The Langmuir trough has provided a measure of particle size, interaction potential and a measure of the hydrophobicity of each compound. The main points from this work are as follows.

(1) The particle diameters are small when compared to conventional colloidal systems (0.1-1μm), and increase linearly with TBN. The number of calcium carbonate and calcium phenate molecules in each of the synthesised inverse micelles was calculated from the experimental data.

(2) The interaction potential between these particles is very close to being a hard sphere, with the 300 TBN particles being marginally more like hard spheres than either the 250 or 150 TBN,

(3) The contact angles obtained indicated that the lower TBN products were in general more hydrophobic than the higher TBN products. Although for the higher TBN adducts (250 and 300) the order depends on the chemical nature of the solvent. The surface tension measurements indicated that the 150 TBN particles are more hydrophobic than other two, but 300 TBN is more hydrophobic than the 250 TBN. The reverse order was found for the 250 and 300 TBN particles on water.

The next chapter is concerned with the atomistic modelling of these detergent systems, used to obtain additional insights into the molecular arrangement of these particles.
Chapter 4. Atomistic Modelling
4.1 Introduction

The experimental techniques described in chapters 2, & 3 were used to characterise the chemical and physical states of the phenate particles, but they were limited in the amount of atomistic detail they could provide. A greater understanding of the microscopic structure of these particles was sought, using the technique of molecular dynamics, MD, atomistic simulation which is the subject of this chapter. The relative numbers of each component obtained, (in part), using the Langmuir trough measurements of chapter 3, were used as input parameters for the computer program, to make the modelled systems as relevant to the real systems as possible. The work reported in this chapter describes simulations of both phenate and sulphonate detergents.

In solution, surfactant molecules self-assemble into micelles, the properties of which are largely determined by the geometric constraints imposed by the shape of the individual surfactant molecules. Aqueous micelles can be spherical, disc-shaped or rod-like depending on the counter ion, and the chemistry of the surfactant head-group and tail. These factors can be combined and rationalised in terms of an effective shape for the surfactant-counter ion pair described by a packing parameter, \( \rho = \frac{v}{\sigma_0 l_c} \), where \( v \) is the volume of the hydrocarbon tail of extended length, \( l_c \), and \( \sigma_0 \) is the area of the head-group. The packing parameter can be used to predict the likely aggregate shape, \( \rho < 1/3 \) for spherical micelles, \( 1/3 < \rho < 1/2 \) for rod-shaped micelles, \( 1/2 < \rho < 1 \) for bilayers and \( \rho > 1 \) for inverse micelles. In the present case, the phenate molecules have \( \rho > 1 \), so we would expect them to form an inverse micelle structure.

To date, molecular dynamics simulations of regular micelles have concentrated on aqueous systems; a common system being that formed out of sodium octanoate. The simulations have shown that the model surfactant molecules naturally assemble
into micelles when started from arbitrary positions. These micelles are stable for at least 100 psec, which is typically the length of the simulation. The model micelles look quite disorganised, and are not the conventional textbook picture of a spherical micelle. Large fluctuations in shape occur about the mean spherical shape. These simulations have shown that there is significant penetration of the solvent in the head-group region. In contrast to the traditional view of a micelle, only a small fraction of the chains were found to be in an all-trans conformation, in fact the gauche vs. trans ratio was statistically the same as for the gas phase molecules. A major discovery of these simulations was that the percentage of trans- conformations in the alkyl chain upon micellisation was statistically the same as for the isolated molecule in the gas phase.

A molecular dynamics study of a highly idealised inverse micelle was performed by Brown and Clarke, who modelled a core of water molecules and ions surrounded by a surfactant coat, itself in a cavity containing some discrete single-centre aprotic solvent molecules. The surfactant molecule was represented by two interaction sites, a cationic head-group and a hydrophobic tail. The inverse micelle structure was stable over a ca. 100 psec simulation, with some fluctuation about the average spherical shape. They found a concentration of anions, head-groups and water molecules in the same radius range from the centre of the micelle. The water molecules were orientationally highly ordered in the boundary region between the core and the hydrophobic region. Some penetration of the water molecules into the hydrophobic region was also observed.

The overbased detergent micelles under investigation in this work are chemically quite different to those normally considered in which the core is predominantly water. With these systems, the core is solid and is made up of (probably amorphous) calcium carbonate with no detectable water. To a much greater extent than water, the CaCO₃ molecules interact strongly with themselves (and with the phenate molecules) through
coulombic interactions. These particles therefore have more in common with colloidal particles, although they are quite small when compared with conventional colloidal systems (2.5 nm vs. typically 100 nm, respectively). The effects of curvature and geometry of the individual surfactant molecules are therefore likely to be more important in determining their properties than in the case of more traditional colloidal particles. In this study, straight single-chained sulphonates are compared with the branched doubly-chained phenates to explore the effect of the surfactant type on the assembled microscopic structure.

This is the first time this technique has been applied to overbased detergents. The simulations were used to help resolve some outstanding uncertainties concerning these systems, including,

- the shape of the micelle,
- the effect of chain length and chemical structure on the effectiveness of the surfactant molecule to stabilise the carbonate core, and
- the effect of solvent on the particles.

A brief description of the techniques employed in this work follows.
4.2 Computational Methods

Atomistic simulations were carried out using the BIOSYM commercial software package. Three types of simulation were carried out:

1. Construction of surfactant molecules, to investigate the effect of chain length and extent of branching.

2. Construction of the inverse micelles *in vacuo* from numbers of surfactant and CaCO$_3$ molecules in ratios determined by the experimental work.

3. Simulations of these micelles were made in a generic hydrophobic solvent medium.

All simulations were carried out on a Silicon Graphics IRIS INDIGO XZ4000 workstation using the BIOSYM packages INSIGHTII and DISCOVER(2.9). INSIGHTII is a graphics based molecular modelling program. Used in conjunction with the molecular mechanics/dynamics package DISCOVER, model molecules were constructed and simulated at thermal equilibrium. Molecular mechanics was used first to minimise the energy of the molecules and approach the global internal energy minimum therefore providing the starting co-ordinates for the molecular dynamics calculations. Molecular dynamics was then performed on these molecules for a period of typically 20 psec until they reached dynamic equilibrium. Reported averages were calculated from periods of further simulation. Production simulations typically lasted for 20 psec, while some extended for more than 50 psec. The accumulated time simulated during the build up to the 300 TBN product was in excess of 500 psec.
4.2.1 Molecular Mechanics

The Molecular Mechanics technique generates the structure of a molecule by incorporating bond length and angle potential energy functions, expressed in terms of differences in the atomic co-ordinates. Non-bonded interactions between atoms, not directly bonded or linked through bending or torsional interactions, are also included in the model. These 'van der Waals' interactions are usually represented by a Lennard-Jones potential with parameters appropriate to each atom type.

The first step in a molecular mechanics calculation is the creation of a table of interatomic distances, bond angles and torsion angles that specify the starting geometry. The values obtained are then used in conjunction with the potential function expressions to calculate an initial 'steric energy', which is the sum of the various component potential energies calculated for the bonds, angles and non-bonded pairs relative to their minimum or equilibrium values.

The computation of this steric energy, along with its first and second derivatives with respect to atomic co-ordinates, enables the geometry of the molecule that has the minimum energy to be found (a procedure called "minimisation"). This provides a molecular structure suitable for harmonic vibrational analysis and subsequent dynamics simulations. The functional form and parameters needed to fit the potential energy surface constitute what is usually referred to as the 'forcefield'.

4.2.2 The forcefield

The 'Constant Valence Forcefield' (CVFF) was employed. The co-ordinates of a molecule combined with the forcefield data create the energy expression for the molecule (eqn. 4-1).
Terms 1-4 represent respectively the energies associated with bond stretching, bending of the 1-2-3 bond angles away from their reference values, rotation of torsion angles by twisting atoms about the bond axis that determines the torsion angle, and distortion of planar atoms out of the plane formed by the atoms they are bonded to. The final two terms in eqn. 4.1 represent respectively the non-bonded interactions, as a sum of repulsive and attractive Lennard-Jones terms, and the Coulombic terms (term 6), all of which are functions of the distance between atom pairs, \( r_{ij} \). The forcefield defines the functional form of each term in this equation as well as the parameters used. Each of the terms in the energy expression will now be considered separately:

**Term 1 Bond Stretching**

The molecule is considered to be a collection of masses held together by Hooke’s law springs. The energy involved in stretching bonds is given by,

\[
E_{\text{stretch}} = \sum_{\text{bonds}} k_b (b - b_0)^2
\]

where \( k_b \) is the bond stretching constant, \( b_0 \) is the ideal bond length and \( b \) is the actual bond length at any instant.
Term 2 Bond Bending

Again a Hooke's law expression is used to represent the energy associated with bending angles from their ideal values,

\[ E_{\text{bend}} = \sum_{\text{bonds}} k_\theta (\theta - \theta_0)^2 \]  

eqn. 4-3

where \( k_\theta \) is the bond bending force constant, \( \theta_0 \) the ideal bond angle and \( \theta \) the instantaneous bond angle.

Term 3 Torsion Angles

The torsion angle between any four bonded atoms \( i-j-k-l \) is defined as the angle between the planes formed by the atom trios \( ijk \) and \( jkl \), which is illustrated in Figure 4.1.

In molecular mechanics the torsional potential is often represented as a truncated Fourier series. The energy due to rotation about torsion angles is represented by a cosine series:

\[ E_{\text{torsion}} = \sum_{\text{tortions}} k_\phi (1 + s \cos(n \phi)) \]  

eqn.4-4

where \( k_\phi \) is the torsional force constant, \( s \) is a phase factor, \( n \), the periodicity and \( \phi \) the torsion angle.
This potential reproduces the various energy maxima and minima as $\phi$ sweeps through $360^\circ$. There are energy maxima for eclipsed conformations, with an overall maximum for the trans case.

**Term 4 Out of Plane interactions (Improper Torsions)**

The improper torsion term implements the resistance to out of plane bending found in organic rings. The improper torsion angle is defined as the angle formed between the components of the bond vectors i-j and l-j that are perpendicular to the bond vector k-j, illustrated in Figure 4.2, and is expressed by a quadratic distortion potential function:

$$E_{\text{out-of-plane}} = \sum_{\text{out-of-plane}} k_\chi \chi^2$$  eqn. 4-5

where, $k_\chi$ is the improper torsional force constant and $\chi$ is the improper torsion angle. It should be noted that although this expression ensures that benzene rings etc. stay relatively flat, it is a mainly non-unique empirical construction.
Term 5 Van der Waals Interactions

Non-bonded short range interactions are referred to here as van der Waals interactions. There is a short range repulsion arising from the electrons in the filled orbitals of atoms trying to avoid overlap (Pauli exclusion principle). This electron pair repulsion is illustrated in Figure 4.3,

![Potential energy curve](image)

Although the analytic form for this potential term is exponential with atom separation, \( r \), it is customary to use an \( r^{-12} \) analytic form, which behaves similarly over typical overlap separations. The second short range force is the attraction that results from the synchronised motion of electrons on the two atoms. (This energy is sometimes called the 'London Dispersion Energy'.) This energy varies inversely with the sixth power of the separation between atoms. The total van der Waals potential energy is the sum of
the attractive and repulsive potential energy terms summed over all non-bonded interactions,

$$E_{vdw} = \sum_{vdw}^{} \frac{A}{r^{12}} - \frac{B}{r^{6}}$$
eqn. 4-6

which is known as the Lennard-Jones potential.\(^6\) This potential is steeply repulsive at short range, attractive at long range, and has a minimum at intermediate distance.

**Term 6 Electrostatics**

The electrostatic interactions are represented by Coulomb's equation,

$$E_{coulomb} = \sum_{coulomb}^{q_iq_j} \frac{q_iq_j}{r_{ij}}$$
eqn. 4-7

where \(\varepsilon\) is the dielectric constant, \(r_{ij}\) is the separation between the charges \(q_i\) and \(q_j\). In the simulation, the charges are either whole numbers of electron charges, \(e\), for the ions (e.g. \(+2e\) for Ca\(^{2+}\)) or fractions of \(e\) for other atoms (these are called partial charges). In the latter case, this represents the distribution of charge within an otherwise neutral molecule.
4.2.3 Molecular Dynamics

Molecular dynamics (MD), generates a time evolution of a molecular system from the intramolecular forces between the atoms and the non-bonded interactions between the molecules. MD is a versatile technique that has been used to model many aspects of liquids and solids. It is classical (as used here) and the atoms move according to the laws of Newtonian mechanics, constrained by the assumed forcefield. Molecular dynamics solves Newton's second equation of motion, \( F_i = m_i a_i \), where \( F_i \) is the force, \( m_i \) is the mass of the atom and \( a_i \) is the acceleration of atom \( i \). The force on atom \( i \) can be computed directly from the derivative of the potential energy \( V \) with respect to the co-ordinate \( r_i \).

\[
F = m_i a_i \quad \text{eqn. 4-8}
\]

\[
-\frac{\partial V}{\partial r_i} = m_i \frac{\partial^2 r_i}{\partial t^2} \quad \text{eqn. 4-9}
\]

Numerical integration of equation 4-9 for each atom enables the system to evolve through time and space. If the position of an atom at time \( t \) is \( r(t) \), then after a short time interval \( \Delta t \) the new position is,

\[
r(t + \Delta t) = r(t) + \frac{\partial r}{\partial t} \Delta t + \frac{\partial^2 r}{\partial t^2} \frac{\Delta t^2}{2} + \ldots \quad \text{eqn. 4-10}
\]

given as a Taylor expansion.

The numerical solution of the equations of motion depends on a knowledge of the position \( r(t) \), the velocity \( \partial r / \partial t \), and the acceleration \( \partial^2 r / \partial t^2 \). The initial co-ordinates are provided from the minimisation stage. Initial velocities are assigned at random from a Maxwell-Boltzmann distribution corresponding to the temperature of interest.
After $r(t + \Delta t)$ in eqn. 4-10 is solved, the original co-ordinates could be replaced with new ones, the velocities updated, and the acceleration recalculated from the new positions. In fact eqn. 4-10 is not used but a development of it is, as described in the next section.

**Integration Algorithm**

If $v_{\text{ave}}$ is the average velocity during the time interval between $t$ and $\Delta t$, then the new position at the end of the interval is,

$$r(t + \Delta t) = r(t) + v_{\text{ave}} \Delta t$$  \hspace{1cm} \text{eqn. 4-11}

The average velocity can be equated to an 'instantaneous' velocity at time $t + \Delta t / 2$,

$$v_{\text{ave}} = v(t + \Delta t / 2),$$  \hspace{1cm} \text{eqn. 4-12}

and this can be calculated using the average acceleration between $(t-\Delta t/2)$ and $(t+\Delta t/2)$:

$$v(t + \Delta t / 2) = v(t - \Delta t / 2) + a_{\text{ave}} \Delta t$$  \hspace{1cm} \text{eqn. 4-13}

If it is assumed that the acceleration is constant between $(t-\Delta t/2)$ to $(t+\Delta t/2)$, then the average acceleration can be set to the instantaneous value at $t$, the mid-point time,

$$a_{\text{ave}} = a(t)$$  \hspace{1cm} \text{eqn. 4-14}

which gives the following equation for the velocity,
\begin{align*}
v(t + \Delta t / 2) &= v(t - \Delta t / 2) + a(t)\Delta t \quad \text{eqn. 4-15}
\end{align*}

Combining eqns. 4-11 and 4-15 gives an equation for updating the co-ordinates,

\begin{align*}
r(t + \Delta t) &= r(t) + v(t + \Delta t / 2)\Delta t \quad \text{eqn. 4-16}
\end{align*}

Equations 4-15 and 4-16 are together known as the \textit{leapfrog velocity Verlet} method.\(^6\)

A key parameter in the Verlet algorithm is the integration time step \(\Delta t\). There are limits on how large the time step can be, which is determined by the highest frequency motion of the system that needs to be incorporated in the dynamical scheme. Fast vibrations imply rapidly changing velocities and accelerations. If the fastest vibration is the C-H stretch (period \(10^{-14}\) seconds), then the time step should be of the order of \(10^{-15}\) seconds. (1 fsec)

\textit{Temperature}

The introduction of realistic temperature effects is one of the main strengths of molecular dynamics over static techniques such as molecular mechanics. The temperature, \(T\), is proportional to the kinetic energy of the system, which can be expressed in terms of the atomic velocities. For a particle of mass, \(m\), and velocity, \(v\), the kinetic energy is given by,

\begin{equation}
K.E = \frac{1}{2}mv^2
\end{equation}

The relationship between temperature, \(T\), and velocity, \(v\), in the classical limit is given by the Maxwell-Boltzmann distribution law,
where \( f(v)dv \) is the probability that a molecule of mass \( m \) has a velocity \( v \) at a temperature \( T \) in the interval \( v \pm dv/2 \). The behaviour of \( f(v) \) as a function of temperature is illustrated in Figure 4.4.6.

\[
f(v)dv = \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-m v^2 / 2kT} 4\pi v^2 dv \quad \text{eqn. 4-18}
\]

Figure 4.4 Maxwell-Boltzmann Distribution

MD initially assigns random velocities to the atoms sampled from a Maxwell-Boltzmann distribution at the desired temperature. The average kinetic energy \( K \) for each molecule of an ideal monatomic gas is proportional to the temperature,

\[
K = \frac{3}{2} k_b T, \quad \text{eqn. 4-19}
\]

where \( k_b \) is the Boltzmann constant. The kinetic energy of an atom is,
\[ K = \frac{3}{2}mv^2. \]  

(4-20)

The factor 3/2 is used because the atom has 1/2k_B T of kinetic energy for each degree of translational freedom in three-dimensional space. An expression for the temperature in terms of velocity is therefore given by \( T = m\langle v \rangle^2/k_b \), where \( \langle v \rangle^2 \) is the mean squared value of \( v \).

It is then possible to compute the temperature for a set of atoms in motion (whether bonded or not) directly from their velocities by taking the mean of the 'atom' temperatures calculated from the above formula,

\[ T = \sum_{\text{atoms}} \frac{m_i v_i^2}{k_b} \]  

(4-21)

The results from the molecular dynamics simulations applied to the model surfactant systems are given in the following section.
4.3 Simulation Results and Discussion

The ability of the phenate to stabilise the carbonate, with a relatively short alkyl chain length (compared to those of the sulphonates), indicates that the conformation adopted by this molecule is likely to be important in determining its effectiveness. Molecular simulations were performed therefore on both the phenate and the sulphonate surfactant types in order to establish the effects of molecular architecture. Initial work was concerned with investigating the isolated surfactant molecules, looking at the effect of chain length and degree of branching on the stability and geometry of these molecules. Examples of these were then selected for subsequent cluster simulations.

4.3.1 Isolated Molecules

The structure and dynamics of the individual surfactant molecules is of some interest because it forms the building unit for the self-assembled structure. Both the phenate and the sulphonate surfactants were built. In the commercial product the chains are branched as indicated in chapter 2. Simulations were performed on straight chain molecules as well the branched ones to explore the effect of branching on the structure of the molecule. The straight chain simulations were also found to provide a useful reference system.

*Straight Chain Molecules*

A series of straight chain molecules (illustrated in Figure 4.5) was constructed *in vacuo*. The first step was to build a *para*-methyl substituted sulphur bridged phenate which was energy minimised at a temperature of 0K using the Molecular Mechanics
method. This optimised structure was then equilibrated at 300K using Molecular Dynamics to thermalise the molecules fully and prepare a state close to that of the molecule in its working environment. Then another methyl group was added, the whole molecule minimised at 0K using molecular mechanics and then molecular dynamics was performed as before. This procedure was repeated by adding one methylene group at a time up to a chain length of C_{12}.

Straight chain sulphonate detergents (Figure 4.5) were also investigated. These molecules are quite different structurally to the phenates in that the surfactants have only one alkyl chain per molecule, whereas the phenates have two chains per molecule. Typically, sulphonates have backbone chain lengths of C_{18} (Figure 4.5(b)). The same simulation procedure was employed as for the straight chain phenate systems.

![Figure 4.5](image)

**Figure 4.5** Structure of straight chain surfactants (a) sulphonate, (b) phenate.

The sulphur bridge of the phenate molecules constrains the geometry of the molecule so that the phenyl rings do not fall in the same plane, but are out of plane by
approximately 20°. This arises from the \(sp^3\) C-S-C bond, which is the pivotal feature in determining the geometry of the whole molecule. Therefore the axes of the two chains are not parallel but there should be a gradual separation between the chain ends with increasing chain length.

During the growth of the alkyl chains between C\(_1\)-C\(_7\), although there were temporary departures from planarity of the molecule, the two alkyl chains were relatively constrained and pointed on average along the axis formed by the ortho-/para- groups of the phenyl ring.

However at C\(_8\) and above, there was a greater tendency for the two alkyl chains to reorientate in opposite directions. The aryl head-group region remained largely undistorted during this realignment of the \(n\)-alkyl chains (e.g. the C-S-C angle changed by less than 1°).

The structural change in the calcium phenate molecule is also manifest in the computed energy of the molecule. For each additional methyl group added to the two chains, there is an increase in the displayed molecule energy. Test simulations performed on simple \(n\)-alkanes had virtually the same energy increment for each additional methyl group. The MD energy (potential plus kinetic) increased from 42.2 kJ mol\(^{-1}\) for CH\(_4\) to 110.9 kJ mol\(^{-1}\) for C\(_4\)H\(_{10}\), with group increment of approximately 25 kJ mol\(^{-1}\) for each methylene group.

The dependence of the MD total energy on the chain length is illustrated in Figure 4.6, which shows the total energy of the molecule increasing almost linearly with chain length, \(n\), with essentially the same increment with each methylene group as for simple alkanes as discussed previously. There is a clear displacement of the graph at ca. C\(_8\). For \(n\) smaller and larger than \(n=8\) the increment in energy is statistically the same. The
'shift' in the energy of the molecule near to C₈ is akin to a first order phase change, which coincides with the 'release' of strain energy within the molecule.

As the length of the chain increases, its end is more free to move around and explore conformational space. This gives rise to a greater number of steric interactions between the two chains as the chains grow, despite them geometrically growing apart because of the skewed relative orientations of the two aryl rings. The 'kink' at C₈ in the energy vs. chain length curve suggests that a structural change has occurred within the molecule. 3D visualisation revealed that, starting at C₈ the geometry of the whole molecule underwent a major structural transformation. The axis of both alkyl chains rotated so that they pointed in almost opposite directions to present a 'splayed' appearance. The aryl part of the molecule hardly changed during this transformation, confirming that this part of the molecule is quite rigid when compared with the alkyl moiety. This would seem to suggest that a chain length of at least C₈ is required for the alkyl chains to be able to form effective stabilising shells, if we assume that the structures formed for n>8 confer a favourable stabilisation. In Figure 4.6 (b) the comparable energy verses chain length curve is shown for the sulphonate system, which is based on two sulphonate chains per calcium ion. As can be seen this curve is almost linear without a discontinuity at a chain length of C₈. Although the longer chains do have a statistical distribution of gauche defects they are not associated with the release of strain energy as is the case for the phenates. Since the chains in the sulphonate molecule are not constrained together, they are far apart and therefore have little interaction with one another.
Computer generated structures for a selection of the molecules are shown in Figure 4.7. Conformations of the n-C₆, n-C₈ and n-C₁₂ and a typical C₁₈ straight chain sulphonate are shown. These molecules are in quite vigorous motion, especially in the alkyl chain region. The longer chains especially oscillate between the extremes (splayed out structure) and conformations in which the chains are almost parallel. Nevertheless, the snapshots are representative of the molecules for most of the time. For the phenates, above C₈ the total energy shows greater statistical fluctuations because of the range of conformational structures that the molecule can explore increases.
Figure 4.6 (a) Total energy verses number of carbon atoms in each chain for the A (straight chain) and B (partially branched chain) phenate molecules, (b) as for (a) except the single chain sulphonates are shown.
Figure 4.7: Computer generated structures showing representative conformations adopted by straight chain phenate molecules. (a) \( C_6 \) phenate, (b) \( C_8 \) phenate and (c) \( C_{12} \) phenate.
Branched Chain Molecules

In Figure 4.8 the chemical structures for the various types of branched chain calcium phenate molecules are shown. The corresponding energies at 300 K are shown in Figure 4.9. While the kinetic energies are independent of isomer for the same total number of carbon atoms, the interaction (or 'steric') energy increases dramatically with the degree of branching. The B structure is probably closest to the straight chain (A) molecule as would be expected from simple steric considerations. As stated in chapter 2, it is this B structure that is closest to the commercial phenate product, therefore all subsequent simulations were performed using the B structure.

A comparison between the chain length dependence of the total energy of the reference straight chain system and that of the B structure is given in Figure 4.6. Above C₄ the two curves increasingly deviate, with the B structure having the more positive energy. As noted previously, a straight chain length of C₈ marks the onset of a departure in the relative chain orientations, which is reflected in a 'kink' in the total energy plot. This also occurs for the branched chain, but at one carbon number higher (i.e., C₉). The corresponding backbone chain length is C₆, which is consistent with the enhanced steric repulsion between the chains derived from the side group methyls. Some representative computer generated structures, illustrating the distortion of the branched chain molecules, are shown in Figure 4.10. It shows that both the straight chain (A) and the branched chain (B) molecules undergo this structural reorganisation of the chains. These representative structures show the tendency for the chains to be directed away from their original axis formed through the para-positions of the phenyl ring, leading to more open structures. The straight chains are more effective in extending through space in this manner than the more compact B structures.
Figure 4.8 Types of branched chain phenate structures.

Figure 4.9 Total energy verses chain structure for the phenate molecules.
Figure 4.10 Computer generated structures showing representative conformations adopted by some B type branched chain molecules. (a) C$_7$ branched chain phenate and (b) C$_{12}$ branched chain phenate.
4.3.2 Cluster Studies in Vacuo

A model 'B' type surfactant was chosen and clustering of these with calcium carbonate was investigated. From the experimental work the relative number of calcium carbonate and surfactant molecules for particular levels of overbasing was determined, and these are given in Table 4.1. Examples I, II and III are in order of increasing base content (150, 250 and 300 TBN respectively).

Table 4.1. Cluster Characteristics determined by experimental and simulation work.

<table>
<thead>
<tr>
<th>Classification</th>
<th>TBN</th>
<th>diameter (total)/ nm</th>
<th>diameter (core)/ nm</th>
<th>Number of CaCO₃</th>
<th>Number of CaPhe</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>150</td>
<td>2.49</td>
<td>0.59</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>II</td>
<td>250</td>
<td>2.95</td>
<td>1.05</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>III</td>
<td>300</td>
<td>3.15</td>
<td>1.25</td>
<td>16</td>
<td>8</td>
</tr>
</tbody>
</table>

The number of each species in clusters I, II and III (given also in the table) were used in the simulations. The simulation procedure was to add one molecule at a time, at an unbiased starting position close to the existing cluster, and then equilibrate this new structure. Additional molecules were added until the correct ratios of carbonate to phenate molecules were achieved for a desired class of particle. It was found that not only the predetermined ratios led to stable structures, but also intermediate ratios led to stable micelles. Therefore there are no 'magic' numbers of building components for this class of cluster, as there are for noble gas clusters. The micelles formed without any biased positioning of the units. The structures adopted were extremely stable over a wide temperature range (300 to 700 K, well within engine operating temperatures). Figure 4.11 shows the total energy of an individual cluster for a range of clusters of differing base content. In Figure 4.11(a) the energy per molecule in the cluster not
discriminating between phenate and carbonate is shown, and Figure 4.11(b) shows the total energy per CaPhe in the cluster, which brings out additional information. The full line on the figure is the computed total energy of the cluster and the dotted line is the predicted energy of the cluster based on a sum of the energies of the component molecules. An individual calcium carbonate molecule has an energy of -2134 kJ mol\(^{-1}\) and the calcium phenate has an energy of -1556 kJ mol\(^{-1}\). From right to left on the figure the relative proportion of carbonate increases, so that the energy per molecule in the cluster goes from the CaPhe to CaCO\(_3\) extremes (Figure 4.11(a)). The two curves show the same qualitative trend, and intersect at a ratio of approximately 0.7, which is below that of the I cluster. For higher relative carbonate content (which corresponds to all synthesised examples) the computed energies are more negative than predicted on a per molecules additive basis (dotted curve). This indicates that the Coulombic interactions between molecules of the same type and interactions between molecules of different types lead to a structure which has a more negative energy than the sum of their individual components. The maximum difference is -61, -218, -230 kJ mol\(^{-1}\) for the I, II and III clusters respectively.

For these overbased micelles, the enthalpic contribution to the Gibbs free energy far exceeds the entropic component. Therefore there is an 'enthalpic' driving force to cluster formation which overrides the unfavourable entropic decrease arising from association of the individual molecules (which is also present for aqueous based inverse micelles). The clusters with the carbonate/phenate ratio of 1 and higher are more thermodynamically stable than the sum of their individual components. Figure 4.11(b) shows the energy per phenate, which becomes more negative as the carbonate loading increases (a commercially desirable objective). For the lowest carbonate/phenate system considered (= 0.5) which would correspond to two phenates to one carbonate, the indication is that this cluster is not thermodynamically stable based on an enthalpic interpretation. In the 1:1 case, two clusters that had the same
carbonate/phenate ratio, but different numbers of individual molecules (2 phenates and 2 carbonates, 4 phenates and 4 carbonates) were considered. These resulted in the same energy per phenate, within the simulation statistical uncertainty, which is always approximately the size of the symbols.

Unlike the individual surfactant molecules, the geometry of these overbased clusters hardly changes with time and was found to be insensitive to temperature within the studied range. This is caused by a combination of strong Coulombic forces in and around the carbonate core, binding these species, and steric hindrance imposed by the proximity of the neighbouring alkyl chains, effectively wedging the surfactant molecules together. The alkyl chains are more immobile, even for the open structure I (Figure 4.12) because the surfactant chains associate over only part of the cluster. Therefore, locally they are sterically hindered. The structure of the 150 TBN (I) cluster does not appear to conform to the spherical geometry normally associated with inverse micelles. This is to be expected, as there are not enough surfactant molecules present to achieve this. The alkyl chains tend to associate over only part of the surface of the core. Figure 4.13 shows the 250 TBN cluster (cluster II), which has a higher carbonate/phenate ratio. As the clusters are built up they naturally self-assemble into non-spherical shapes, which are flat and discus shaped. The carbonate is in the core and the surfactant forms a shell around it. If these structures are the most stable naturally occurring forms it would imply that the core is exposed on two sides to the solvent. Interestingly, some of the chains project out of the plane of the cluster, departing somewhat from the discus shaped structure. Figure 4.14 shows the 300 TBN cluster (cluster III), which is very similar to cluster II except that the phenate clusters are more tightly packed around the equator of the cluster, presenting a more 'ellipsoidal' shape. There is a greater tendency for the chains to extend over and cover the exposed part of the core (where there is considerable free space) providing more protection for the inorganic species from any solvent.
The cluster core and total diameters of the overbased phenates are known from previous Langmuir trough measurements. I estimated the equivalent sphere radii as those of the maximum area projections. These are given in Table 4.2. For the more overbased clusters, there is more carbonate in the core which swells the clusters. For clusters II and III a disc projection was used and for cluster I a triangle, as in this case there are few molecules. The agreement with experiment is very good, especially for the higher TBN clusters (II & III). However this could be fortuitous as there are a number of ambiguous factors. For example, these clusters are certainly not spherical, which is assumed in the Langmuir trough interpretation. However, in the absence of any ordered liquid crystalline arrangement it is likely that the clusters are randomly oriented on the water surface in the Langmuir trough experiment so an average particle size is almost certainly measured.

Admittedly the environment on the trough is in marked contrast to the normal environment of these clusters (i.e. in a hydrophobic solvent). Previous neutron scattering of these phenates has shown that they are smaller on the trough surface than in a hydrophobic solvent.

**Table 4.2 - Cluster Characteristic diameters, D, determined by (a) experiment and (b) simulation.**

<table>
<thead>
<tr>
<th>Structure</th>
<th>( D_a ) core /nm</th>
<th>( D_a ) total /nm</th>
<th>( D_h ) core /nm</th>
<th>( D_h ) total /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.59</td>
<td>2.49</td>
<td>0.61</td>
<td>1.85</td>
</tr>
<tr>
<td>II</td>
<td>1.05</td>
<td>2.95</td>
<td>1.03</td>
<td>2.85</td>
</tr>
<tr>
<td>III</td>
<td>1.25</td>
<td>3.15</td>
<td>1.26</td>
<td>2.90</td>
</tr>
</tbody>
</table>
Figure 4.11 The average computed total energy for various sized clusters. The clusters I-III considered for special attention in the text are indicated on the figure. (a) shows the total energy of the cluster per molecule, not discriminating between carbonate and phenate and (b) shows the total energy per phenate molecule in the cluster.
Figure 4.12 Ball and stick projections of typical conformations adopted by cluster I (2 CaPhe and 2 CaCO$_3$) during the simulation. (a) and (b) show two approximately orthogonal projections.
Figure 4.13 as for Figure 4.12 except that cluster II (6 CaPhe and 10 CaCO$_3$) is considered and shown as a space fill projection.
Figure 4.14 as for Figure 4.12 except that cluster III (8 CaPhe and 16 CaCO$_3$) is considered.
Sulphonate cluster calculations were also carried out using the same procedure as for the phenates, by adding carbonate and surfactant molecules in the same ratio as for the phenates. An individual Ca(sulph)\(_2\) molecule had an energy of -282 kJ mol\(^{-1}\) as compared with -1556 kJ mol\(^{-1}\) for the Ca(Phe) molecule. i.e. the sulphonate molecule has a more positive energy which can largely be attributed to the length of the alkyl chain. However, it is not so much the absolute energy that is important here, but whether these molecules assemble into a cluster which has a lower energy than the sum of the individual energies, and if this is the case this difference in energy is a measure of the thermodynamic stability of the system. The energy per sulphonate molecule vs. the ratio of carbonate/sulphonate is plotted in Figure 4.15, which shows that the energy per sulphonate molecule is more negative than predicted on the basis of the summation of the individual component molecules. The two curves do however show the same trend and intersect at a ratio of approximately 0.25 (cf. phenates 0.8) which would correspond to four sulphonate molecules and one calcium carbonate molecule, implying that below this ratio the cluster would be thermodynamically unstable. As the sulphonate head groups are not attached to one another, they are more mobile and can therefore more readily form more stable (negative energy) structure than the phenates, where the two O\(^-\) atoms are constrained at fixed distances from each other. Figure 4.16 shows some snapshots of sulphonates.

In terms of base number, this ratio would correspond to approximately 25 TBN, whereas for the phenates the crossover occurs at approximately 100 TBN. In practice, sulphonates can be synthesised to lower TBN than the phenates and this result would seem to provide some basis for this.

Figure 4.16(a) shows the least overbased sulphonate cluster, consisting of one sulphonate and one carbonate molecule. This is formed by adding a calcium carbonate molecule to the molecule shown in Figure 4.5. The effect is to force together the surfactant chains. The phenate cluster is more wedge shaped, whereas in the
sulphonate there is more complete coverage of the carbonate core. The aryl rings are not joined together in the sulphonate so that there is greater freedom for the cluster to organise in a more spherical shape. This trend continues up to the equivalent of the 250 TBN phenate (cluster II), shown in Figure 4.16(b). The chains are longer than for the phenates, so they are better at bending over and covering the core. In practice sulphonates are typically larger than phenates, with chains lengths of $C_{15}$-$C_{36}$. Core diameters of 2.2 and 6.7 nm were obtained and a shell thickness of 1.9 nm. Presumably this is because of the major geometrical differences between the sulphonate and phenate surfactant types. The phenate is more of a conventional inverse micelle forming surfactant (such as AOT), whereas the sulphonate is a conventional straight chained surfactant.
Figure 4.15 The average computed total energy per sulphonate molecule for the various sized sulphonate clusters.
Figure 4.16 Ball and stick projections of typical conformations adopted by sulphonate clusters. (a) 1 Ca(C\textsubscript{18}H\textsubscript{37}SO\textsubscript{3})\textsubscript{2} and 1 CaCO\textsubscript{3}, and (b) 6 Ca(C\textsubscript{18}H\textsubscript{37}SO\textsubscript{3})\textsubscript{2} and 10 CaCO\textsubscript{3}
In order to look at the structure of these micelles in more detail, some radial distribution functions (or pair distribution functions, PDF, \( g(r) \)) of the 250 TBN phenate micelle were looked at. The particles are held together by intermolecular forces, but their kinetic energies give rise to some flexibility in the structure, resulting in the whole structure being mobile. The best description of the average locations of the particles can be obtained from the PDF's. Taking the centre of an atom as the origin, this \( g(r) \) gives the probability of finding the centre of another atom at the end of a vector of length \( r \) drawn from the origin. In a crystal, \( g(r) \) is a series of sharp spikes representing the certainty that particles lie at definite locations, and this regularity continues out to large distances i.e. indicating \textit{long-range order}. However when the crystal melts this long-range order is lost. Close to the first particle there is some order because the positions of the neighbours are correlated with it (\textit{short-range order}).

The PDF's for the 250 TBN phenate and sulphonate are shown in Figure 4.17, and are almost identical. The regular co-ordination is evident, but the fact that the maxima are damped out at larger interatomic distances reflects the fact that there are many more possibilities for the pair as one travels outward from any centrally chosen atom. As can be seen there is a large peak at 2.40 nm. EXAFS studies performed on sulphonate systems show the micelle core is comprised of amorphous calcium carbonate, with each calcium ion being surrounded by 5.9 oxygen atoms at a distance of 2.40 nm. In the \textit{crystalline} form of calcium carbonate, the co-ordination number is 6 at a distance of 2.365 nm. With the diagnostic tools available, it was not possible to distinguish between a crystalline and amorphous structure. However, visual inspection of the core (Figure 4.18) indicated that they showed no evidence of internal symmetry, so an amorphous structure appears to be consistent with previous experimental work.\textsuperscript{70,71}
Figure 4.17 Radial distribution function for Ca-O in (a) 250 TBN phenate and (b) equivalent 250 TBN sulphonate.
Figure 4.18 Snapshot showing the core of the 250 TBN phenate (cluster II).
4.3.3 Overbased Clusters in Hydrophobic Solvent

All simulations up to this point were performed in vacuo. This is an interesting state as the powdered adduct is clearly an important intermediate stage in analysis. However, the real detergent particles are used commercially when dispersed in a paraffinic solvent (mainly C$_{12}$ straight chains). In order to assess the effect of the solvent on the structures of the micelles, simulations were performed on the 250 TBN model phenate (cluster II) in a cloud of solvent. (Computational limitations prevented a more complete representation of the solvent to be employed). Owing to limitations in available computational resources, a model n-hexane solvent was employed, which was considered a reasonable compromise. It is doubtful whether the cluster is significantly influenced by the long chain nature of the solvent molecules beyond C$_6$, rather by local segment interactions which are likely to be similar in hexane and dodecane. (The molecule chosen must be a liquid at room temperature.) The procedure was to build a box of these solvent molecules (shown in Figure 4.19), equilibrate it for 100 psec at 300 K in the absence of periodic boundaries. The cluster was then immersed in this liquid drop. Further equilibration for 100 psec was undertaken, then further analysis and snapshot configurations were stored for presentation.

In Figure 4.20 the effect of the hydrophobic solvent on the structure of the cluster is shown. For clarity I show the cluster omitting the solvent molecules in Figure 4.20(b) and just the solvent molecules in Figure 4.20(c) viewed in the same projection and from the same 'snapshot' configuration. Comparison with the corresponding vacuum cluster (Figure 4.20(a)) indicates that the solvent does have a strong effect in opening out the chains so that it presents more of a 'bow-tie' shape rather than a discus. The solvent molecules penetrate between the chains of the phenate, swelling that part of the cluster. The chains bend out of the plane when compared with the vacuum case. The carbonate core and aryl part of the surfactant appear to be largely unaffected by
this (although the diagnostic tools available were somewhat limited in this respect). The important point here is that the solvent has some effect on the structure of the cluster, and with a more complete solvent soak I would expect this trend to continue. However, I would be surprised if the phenate micelles became spherical, even if simulated with a realistic solvent and a complete soak. Even in the vacuum, the sulphonates are spherical, so there does appear to be a strong inclination for the phenates to adopt a non-spherical structure, which is quite different from the sulphonates.

Figure 4.19 Solvent (n-Hexane) starting box.
Figure 4.20 Cluster projections: (a) a cluster II sideview (simulation performed in vacuo), (b) a cluster I sideview in the presence of solvent and (c) as for (b) but only showing the solvent molecules.
4.3.4 Co-surfactant Studies

Co-surfactants are widely used in micellar systems, as they can have an effect on the size and shape of the micelles. Micelles can even undergo a phase inversion i.e. change from an oil-in-water system to a water-in-oil system by the addition of n-alkanols. As previously mentioned at the beginning of the chapter, the shape of a micelle is governed by the packing parameter, \( \rho \), where \( \rho = \frac{\nu/a_0}{l_c} \). \( \nu/l_c \) is the effective cross sectional area of the chain, \( a_c \). The greater this area the greater is the packing parameter. The addition of rod-shaped co-surfactants (single chained and with compact head groups) decreases the surface curvature and therefore the value of \( \rho \).

In the case of inverse micelles, the presence of co-surfactants enables larger cores to be achieved. It is possible therefore that in the overbased systems, the presence of a co-surfactant could lead to larger cores and hence higher TBN values. In order to explore this hypothesis a series of simulations were performed. A C\(_{18}\) straight chained calcium stearate molecule was built and equilibrated using molecular mechanics and molecular dynamics as before. These surfactant molecules were then introduced into the structure of the 250 TBN phenate cluster and simulation performed. An interesting effect was observed, whereby the molecules of calcium stearate wedged themselves between the molecules of the phenate surfactants effectively swelling out the structure. (see Figure 4.21) These co-surfactants have small head groups in relation to the phenate and therefore it is still possible for the headgroups to penetrate the already crowded part of the micelle. This could have implications for the maximum extent of overbasing that it is possible to achieve using these types of surfactants. These results indicate that there is a bigger void in the core as a result of co-surfactant inclusion in the particle and possibly allows for the further inclusion of calcium carbonate molecules i.e. increasing the extent of overbasing. This could have very important industrial consequences as inclusion of co-surfactants with the existing phenate surfactants could improve the performance of the product.
It is interesting that the co-surfactant goes where it does, rather than in the relatively exposed part of the particle. There is an excess of positive charge in that region of the core, and therefore it is reasonable that the negatively charged stearate head group should be attracted to this region, despite the surfactant crowding that will occur.

It should be noted however, that these findings are based on a few simulations and it would be interesting to carry out further simulations of this type. This will be discussed further in chapter 6.
Figure 4.21 Snapshot showing the effect of co-surfactants on the structure of the 250 TBN phenate cluster.
4.4 Summary

This chapter has shown that the technique of computer simulation can be used to gain very useful information on the microstructure of overbased detergent systems. It is unique in providing a complete atomistic description of these systems. The main conclusions are summarised below.

1. There is some evidence that in the case of the phenate surfactant types, a chain length of at least C₈ may be required to form an effective stabilising shell.

2. When these phenate surfactants are put together with calcium carbonate, an inverse micellar structure is formed, with the carbonate at the centre and the phenate molecules forming a shell around these, the dimensions of which are comparable to those particle sizes obtained from the Langmuir trough work. However, the shape of the cluster is not spherical but disc-shaped, with the surfactant molecules forming a plane around the centre. The implications of this are that there are two exposed sides of carbonate on either side of the micelle. Interestingly, these inverse micelles are very stable with time, which is different to conventional water containing inverse micellar systems, where fluctuations in shape occur as the simulation proceeds. Temperature has a small effect on the structure of these clusters, which is important as they have to operate at engine temperatures.

3. The effect of solvent on these systems was looked at by the introduction of a hydrocarbon solvent (hexane) which resulted in the opening out of the surfactant chains, effectively swelling the micelle. Therefore the solvent does have an effect on the overall shape of the micelle.
4. The corresponding sulphonate clusters were spherical in shape rather than disc-shaped. This could be explained by the fact that these surfactants are not constrained to the same extent as the phenates, giving them a greater freedom to form a uniform coat around the core. The geometry of the surfactant therefore has a marked effect on the overall shape of the inverse micelle.
Chapter 5. Bulk Properties
5.1 Introduction

One of the most important physical properties of colloidal dispersions is the tendency for the particles to aggregate. There is a lot of evidence that inorganic species form large clusters. Kandori et al. have shown that BaCO$_3$ and CaCO$_3$ containing reverse micelles of 1,2-bis-(2-ethylhexyloxy carbonyl) form particle diameters ranging from $400\,\text{Å} \rightarrow 1500\,\text{Å}$. These particles are much larger than those from the micelles from which they were initially formed, thus indicating that the initial carbonate clusters amalgamate at later times. Encounters between particles dispersed in a liquid medium occur frequently and the stability of a dispersion is determined by the interaction between the particles during these encounters. When particles aggregate together many different shapes can be formed which do not necessarily correspond to the shape of the primary particles. Some form of attractive force is required to cause aggregation. To counteract this and promote stability, short range repulsive forces are required to prevent the particles approaching too closely and being "captured" by the attractive forces. There are a number of types of interaction that can lead to aggregation (all electrostatic in origin).

1. Two molecules with permanent dipoles mutually orientate in such a way that attraction results, so-called dipole-dipole attraction.

2. Dipolar molecules induce dipoles in other molecules so that attraction results.

3. Attractive forces operate between non-polar molecules - this is termed London's 'dispersion force' and is due to the polarisation of one molecule by fluctuations in the charge distribution in a second molecule. These dispersion forces are the van der Waals forces. These are the principal attractive forces that lead to aggregation in polymer colloidal systems.
In colloidal dispersions the distribution of atoms/particles is determined largely by the fact that they do not overlap physically *i.e.* they do not interpenetrate. The equilibrium properties are governed by the concentration of particles in the dispersion and by the interaction between the particles - repulsive forces giving rise to stable dispersions, attractive forces giving rise to unstable dispersions. Strong repulsive forces can give rise to ordered iridescent phases, whereas strong attractive forces between the particles can cause the particles to flocculate.

There are a number of experimental techniques available to study the effect of aggregation including light scattering, rheology, sedimentation, ultra-centrifugation. In this chapter rheology, light scattering and dielectric measurements were made to characterise the bulk states of the additives and their results are discussed.
5.2 Dielectric Spectroscopy

Dielectric spectroscopy is a convenient technique for the non-invasive examination of heterogeneous systems e.g. emulsions, gels.\textsuperscript{75,76} The technique has also been used to determine the relaxation processes and percolation behaviour of colloidal suspensions and polymeric systems.\textsuperscript{77-83}

When a solution of colloidal particles in a poorly conducting solvent is placed between electrodes and subjected to an alternating electric field, it has the possibility to conduct and also to become polarised. The relative extents to which these will occur will depend on the frequency, $\omega$. At high frequencies the polarisation of the particles will dominate and conduction will be at a minimum. As the frequency decreases the charge carriers (i.e. the colloidal particles) will have more time to transfer charge between them in a cycle, as a result of self-diffusion and consequently the conduction of the solution will increase. This increase in conduction as the frequency decreases can be used as an indirect measure of the self-diffusion coefficient, $D$, of the colloidal particles and, by using the Stokes-Einstein equation, the effective diameters of the charge carriers. If the inverse carbonate micelles aggregate to any significant extent, this should be reflected in the size of the charge carrier, i.e. the aggregate being much greater than the individual cluster (the subject of my discussion up to now).

2.1.1 Theory

The technique measures the capacitance and conductance as a function of frequency. The dielectric constant $\varepsilon'$ is derived from the measured capacitance, $C$,

$$\varepsilon' = \frac{Cd}{A\varepsilon_0}$$  \hspace{1cm} \text{eqn. 5-1}
where $A$ is the area of the plates, $d$ is the inter electrode distance and $\varepsilon_0$ is the permittivity of a vacuum.\textsuperscript{84} The dielectric loss constant $\varepsilon''$ is derived from the measured conductance $G$,

$$\varepsilon'' = \frac{Gd}{2\pi\omega A \varepsilon_0} \quad \text{eqn. 5-2}$$

The phase angle, $\delta$ is defined as $\tan^{-1} (\varepsilon'/\varepsilon'')$,\textsuperscript{85}

$$\delta = \tan^{-1} \left( \frac{2\pi\omega C}{G} \right) \quad \text{eqn. 5-3}$$

A graph of log frequency verses phase angle shows an inflexion at 45°. The frequency corresponding to a phase angle at 45° is termed the 'critical frequency', $\omega_c$, and at this frequency the processes corresponding to the real and imaginary parts of the permittivity of the system are equal. This is the point at which substantial charge transfer starts to occur by virtue of particle diffusion. This critical frequency increases with increasing concentration because there is a greater diffusional collision rate between the suspended particles as a result of their closer proximity, thus increasing the level of bulk charge transfer. At this critical frequency the charge can "hop" from one particle to another, and therefore from one electrode to the other in the period of a cycle.

The velocity of individual particles is continually changing direction as a result of random collisions with the other molecules. When certain of the particles in the system are much larger than others, i.e. with a dispersion of micelles, then the motion of these 'suspended' particles can be described by 'Brownian motion'. Treating Brownian motion as a 3-D random walk, the mean displacement, $\mathbf{X}$, after time $t$ is given by the Einstein relation,\textsuperscript{86}
\[ x = (2D \tau)^{1/2} \]  
\text{eqn. 5-4}

where \( D \) is the self-diffusion coefficient. The mean time scale corresponding to the characteristic frequency, \( \omega_c \), is given by,
\[ \tau = \frac{2\pi}{\omega_c} \]  
\text{eqn. 5-5}

where \( \omega_c \) is the characteristic frequency. Equation 5-4 then becomes,
\[ x = 2 \left( \frac{2\pi}{\omega_c} \right)^{1/2} \]  
\text{eqn. 5-6}

The diffusion coefficient of a suspended material is related to the friction coefficient, \( f \), by Einstein's law of diffusion, \( Df = kT \), and since \( f = 6\pi a \eta \) (Stokes' relation), we have,
\[ D = \frac{kT}{6\pi a \eta} \]  
\text{eqn. 5-7}

where \( k \) is the Boltzmann constant, \( a \) is the particle radius and \( \eta \) is the viscosity of the solvent. This is called the Stokes-Einstein relationship.\(^8^7\)

If the particles of radius \( a \) and volume fraction \( \phi \) are assumed to be in a cubic close-packed arrangement the distance between the particle centres, \( h \), is given by,
\[ \frac{h^3}{a^3} = \frac{4\pi}{3\phi} \]  
\text{eqn. 5-8}

From this the separation between the particle surfaces, \( s \), in the cubic arrangement can be expressed as,
\[ s = \left[ \left( \frac{4\pi}{3\phi} \right)^{1/3} - 2 \right] a \]  
\text{eqn. 5-9}
where $1/\Phi$ is equal to the volume dependent term in square brackets in equation 5-9. If $s$ from eqn. 5-9 is equated with $X$ from eqn. 5-6, then the characteristic frequency can be related to the radius, $a$, of the particle by the following equation,

$$\omega_c = \frac{2kT\Phi^3}{3\eta a^3}$$

eqn. 5-10

This equation is used to interpret the dielectric spectroscopy data. Measurement of the characteristic frequency at a known micelle volume fraction in a solvent of known viscosity allows the effective size of the detergent unit, $a$, to be determined. This enables an estimate of the number of basic micelle clusters in each charge carrying unit to be calculated.
5.2.2 Dielectric Results
The experiments were performed using a 'Wayne-Kerr 6425 Precision Component Analyser'.

The active components were isolated from the oil using the procedure described in chapter 2. Aggregate size depends on a number of factors,

(i) the concentration of the adduct,
(ii) the TBN, and
(iii) the chemical nature of the solvent.

(i) Concentration

The powdered 250 TBN adduct was considered for most of this phase of the work. The range of concentrations considered is given in Table 5.1. Figure 5.1 shows the variation in the phase angle with frequency as a function of concentrations. This data was used to determine the critical frequency and from eqn. 5-10, diameters. Table 5.1 also gives the derived particle diameters. It should be noted that the sizes obtained using this method are much larger than those obtained from the Langmuir trough method (chapter 3) giving evidence that these particles do have a tendency to form quite large aggregates. As the concentration is increased so does the effective particle diameter, although the relationship is not linear. Figure 5.2 shows how the particle diameter varies with concentration. At concentrations of approximately 20% w/w it can be seen that the particle size increases rapidly. This can be considered to coincide with a 'percolation point' of the system at which the aggregates themselves form one large aggregate or network spanning the system. The fact that the aggregate size increases with concentration can be attributed to the relative proximity of the particles, increasing not only the charge transfer, but also the extent of aggregation.
This level of aggregation was considered surprising. It is possible that the procedure of separating the active detergent from the base oil into a powder, could have been responsible for some agglomeration of the micelle particles, which persisted in the re-dispersed system. In order to discover if this was so, the behaviour of the additive in the original base oil was explored without going through the adduct (i.e. powder) stage. Here the sample was simply diluted in toluene and the experiments performed as for the re-dissolved adduct. Figures 5.3 shows the phase angle vs. frequency graph for the diluted adduct. Figure 5.4 gives the particle size vs. concentration graphs. The particle sizes obtained shown in Table 5.2 are still very large (average 280 Å), but there does not appear to be quite the same dependence of particle size with concentration as was found for the extracted adduct systems. The number of basic micelle units was estimated (given in Tables 5.1 & 5.2) by dividing the theoretical volume of the aggregate (assuming that the aggregate structure formed is spherical) and dividing this by the micelle volume based on the particle radii from the Langmuir trough work. As can be seen, there are a large number of the basic micelle units in the aggregates. This will be the upper limit on the number of basic micelle units, as the aggregates could be fractal open structures.

(ii) TBN

150 and 300 TBN materials were also investigated in their extracted form. Concentrations in the range 1-20 % w/w were looked at. Figures 5.5 and 5.6 show the phase angle vs. frequency curves for the 150 and 300 TBN samples respectively. The calculated sizes are shown in Tables 5.3 and 5.4. Figure 5.7 shows the dependence of the particle diameter on the concentration for these two systems. As can be seen the particle sizes are very similar for all the TBNs considered. For a system to percolate, pairs of particles must have shells which overlap. Therefore particles with a greater
shell/core ratio have a greater probability for pair-wise overlap. If this were true for these overbased systems, the lower TBN sample would have the greatest particle diameter. The number of basic micelle units was calculated as for the 250 TBN adduct and the results are given in Tables 5.3 & 5.4. For the same concentration (%wt) the 150 TBN aggregates have the greatest number of basic units followed by the 250 TBN then the 300 TBN. One explanation for this is that the molecular weight for the 150 TBN system is lower than that of the 250 or 300 TBN particles, so that there are more 150 TBN micelles per unit volume than for the higher TBN samples. It is also possible that there is greater attraction between the particles in the lower TBN samples. This technique has highlighted the fact that the aggregate size is not dependent on the TBN, but the number of micellar units could be dependent on the TBN.

**(iii) solvent.**

I also investigated another solvent to discover if the level of aggregation was affected by the chemical nature of the host fluid. Dodecane was chosen as an alternative to toluene, as the adducts are soluble in both. Dodecane is also chemically quite similar to the base oil in which the adduct is found in commercial applications. Figure 5.8 shows the phase angle vs. frequency for the range of concentrations. The particle diameters are given in Table 5.5 along with the concentrations. These sizes were then plotted against the concentration (see Figure 5.9) and the behaviour is similar to that found for toluene, except that the diameters are larger. These solvents have a very low relative permittivity (2.39 for toluene and 2.02 for dodecane at 20°C). It is possible that the mechanism by which the individual micelle particles agglomerate is by electrostatic attraction between the cores. The range of attraction could be quite large as the solvent has a low permittivity. The experimental data is consistent with this hypothesis, as the toluene agglomerates are somewhat smaller than those formed in dodecane. The
range of attraction will be larger in dodecane because it has a smaller relative permittivity and therefore has only a limited ability to moderate the forces of electrostatic attraction.\textsuperscript{89}

Another possible reason for this reduced attraction in toluene could be due to the chemical similarity between the dodecane and the alkyl chains in the phenate. Ordering or 'freezing' of the solvent molecules near the particle surface might occur and thus cause the total attraction to increase. The stabilising chains of the particles are very similar to the chains of dodecane and therefore they might induce an extra 'bridging-type' interaction between the particle surfaces. This was shown to be the case for silica particles coated with octadecyl chains.\textsuperscript{90} In good solvents the interactions are repulsive because the chain segments prefer contacts with the solvent molecules than to the chains of other particles, whilst in bad solvents the situation is reversed.\textsuperscript{91,92} The number of micellar units is also given in Table 5.5 and these are greater in dodecane than in toluene, confirming the increased attraction between the particles in dodecane.

Those results suggest that the detergent particles have strong attractive forces which causes them to flocculate. Although the mechanism of flocculation is not really known at this stage (electrostatic interactions between the cores or association facilitated by the solvent molecules or some other mechanism). It has been found that the choice of the solvent can have an effect on this. It is likely that these particles will aggregate in oil. The effect this might have on the physical properties of the oil is the subject of the next section.

This technique has brought to light the tendency of these systems to aggregate (in solution) and has given some measure of the aggregate size and what affects this. However, it does not tell anything about the strength of the attraction between the particles. Rheological measurements were made to attempt to gain information on the strength of this attraction in the neat samples. The results of these measurements are discussed in the next section.
Table 5.1 Dependence of calculated parameters on concentration for the 250 TBN adduct dissolved in toluene.

<table>
<thead>
<tr>
<th>Concentration /%wt</th>
<th>Effective particle diameter /Å (±5Å)</th>
<th>No. basic micelle units in the aggregate</th>
<th>( \omega_c /\text{Hz} )</th>
<th>( \tau /10^{-3} \text{s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.01</td>
<td>628</td>
<td>9647</td>
<td>4450</td>
<td>1.40</td>
</tr>
<tr>
<td>4.99</td>
<td>638</td>
<td>10115</td>
<td>21250</td>
<td>0.30</td>
</tr>
<tr>
<td>9.99</td>
<td>664</td>
<td>11403</td>
<td>47000</td>
<td>0.13</td>
</tr>
<tr>
<td>20.54</td>
<td>824</td>
<td>21793</td>
<td>89000</td>
<td>0.07</td>
</tr>
<tr>
<td>30.47</td>
<td>1132</td>
<td>56503</td>
<td>97500</td>
<td>0.06</td>
</tr>
<tr>
<td>40.01</td>
<td>1716</td>
<td>196827</td>
<td>85000</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Table 5.2 Dependence of calculated parameters on concentration for the 250 TBN neat sample diluted in toluene

<table>
<thead>
<tr>
<th>Concentration /%wt</th>
<th>Effective particle diameter /Å (±5Å)</th>
<th>No. basic micelle units in the aggregate</th>
<th>( \omega_c /\text{Hz} )</th>
<th>( \tau /10^{-3} \text{s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.98</td>
<td>662</td>
<td>11301</td>
<td>3675</td>
<td>1.71</td>
</tr>
<tr>
<td>4.99</td>
<td>530</td>
<td>5799</td>
<td>37321</td>
<td>0.17</td>
</tr>
<tr>
<td>9.41</td>
<td>568</td>
<td>7138</td>
<td>69000</td>
<td>0.09</td>
</tr>
<tr>
<td>18.63</td>
<td>706</td>
<td>13707</td>
<td>116000</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Table 5.3 Dependence of calculated parameters on concentration for the 150 TBN adduct sample diluted in toluene

<table>
<thead>
<tr>
<th>Concentration /%wt</th>
<th>Effective particle diameter /Å (±5Å)</th>
<th>No. basic micelle units in the aggregate</th>
<th>ωc /Hz</th>
<th>τ /10^-3 s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.98</td>
<td>578</td>
<td>12508</td>
<td>5500</td>
<td>1.11</td>
</tr>
<tr>
<td>4.91</td>
<td>294</td>
<td>13576</td>
<td>26000</td>
<td>0.24</td>
</tr>
<tr>
<td>9.59</td>
<td>646</td>
<td>17462</td>
<td>48000</td>
<td>0.13</td>
</tr>
<tr>
<td>20.01</td>
<td>800</td>
<td>33164</td>
<td>90000</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Table 5.4 Dependence of calculated parameters on concentration for the 300 TBN adduct sample diluted in toluene.

<table>
<thead>
<tr>
<th>Concentration /%wt</th>
<th>Effective particle diameter /Å (±5Å)</th>
<th>No. basic micelle units in the aggregate</th>
<th>ωc /Hz</th>
<th>τ /10^-3 s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.01</td>
<td>612</td>
<td>7334</td>
<td>4800</td>
<td>1.31</td>
</tr>
<tr>
<td>5.02</td>
<td>592</td>
<td>6638</td>
<td>26800</td>
<td>0.23</td>
</tr>
<tr>
<td>9.99</td>
<td>636</td>
<td>8231</td>
<td>53500</td>
<td>0.12</td>
</tr>
<tr>
<td>19.97</td>
<td>798</td>
<td>16258</td>
<td>92000</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Table 5.5 Dependence of the calculated parameters on concentration for the 250 TBN adduct sample diluted in dodecane.

<table>
<thead>
<tr>
<th>Concentration /%wt</th>
<th>Effective particle diameter /Å (±5Å)</th>
<th>No. basic micelle units in the aggregate</th>
<th>ωc /Hz</th>
<th>τ /10^-3 s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.10</td>
<td>736</td>
<td>115530</td>
<td>955</td>
<td>6.58</td>
</tr>
<tr>
<td>4.09</td>
<td>772</td>
<td>17992</td>
<td>5900</td>
<td>1.06</td>
</tr>
<tr>
<td>10.06</td>
<td>818</td>
<td>21320</td>
<td>12200</td>
<td>0.50</td>
</tr>
<tr>
<td>20.01</td>
<td>992</td>
<td>38025</td>
<td>21000</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Figure 5.1 Phase angle vs. frequency plots as a function of concentration for the 250 TBN adduct in toluene.

Figure 5.2 Particle diameter vs. concentration for 250 TBN adduct in toluene.
Figure 5.3 Phase angle vs. frequency as a function of concentration for the 250 TBN neat additive diluted in toluene.

Figure 5.4 Particle diameter vs. concentration for the 250 TBN neat additive diluted in toluene.
Figure 5.5 Phase angle vs. frequency plots as a function of concentration for the 150 TBN adduct in toluene.

Figure 5.6 Phase angle vs. frequency plots as a function of concentration for the 300 TBN adduct in toluene.
Figure 5.7 Particle diameter vs. concentration for 150 and 300 TBN adducts in toluene.
Figure 5.8 Phase angle vs. frequency plots as a function of concentration for the 250 TBN adduct in dodecane.

Figure 5.9 Particle diameter vs. concentration for 250 TBN adduct in dodecane.
5.3 Rheology

Rheology is concerned with the flow and/or deformation of matter under the influence of externally imposed strain (often shear).\textsuperscript{93,94,95} A characteristic of solids is that they respond to a small external strain by deforming, and on removal of the strain they return to their original shape. Such a response is termed elastic. In the simplest case the stress is proportional to the deformation. In the case of a fluid, if an external strain is applied it deforms and continues to deform as long as the strain is increased. The removal of this strain will not result in a return of the fluid to the undeformed state where the molecules are in their original positions. This type of response is called viscous flow. The fluid will deform under external stresses but internal frictional forces will cause it to lose "memory" of its original state and the molecules will stay far from their original positions.

There are however materials which are neither purely elastic nor purely viscous and they are called \textit{viscoelastic} materials. These substances may be either viscoelastic solids which exhibit some viscous effects during deformation, or fluids which exhibit some elastic effects. To characterise the rheology of a liquid it is usually necessary to carry out a range of different types of rheological experiment. A continuous deformation ("shear") rate is used to determine the shear rate dependence of the viscosity and the Newtonian viscosity (i.e. the viscosity in the limit of zero shear). Oscillatory shear rate experiments are carried out to measure the frequency dependence of the viscosity and hence the viscoelasticity. These experiments were carried out on the neat additive, as the low viscosity of the dilute solution led to measurement problems, as the angular velocity of the system was too high.
5.3.1 Experimental

All measurements were carried out using a 'Carrimed Constant Stress Rheometer'. The liquid is confined between two surfaces which move relative to one another and thereby shear it. There are two different types of shearing geometry available, cone and plate and concentric cylinders. The cone and plate method is used for very viscous materials which are not likely to be ejected out of the sides of the device. Most fluids have to be confined in a concentric cylinder geometry as they would not stay within the cone and plate arrangement.

Cone and Plate

The apparatus is illustrated in Figure 5.10 (a). It consists of a truncated cone of radius R, with its axis perpendicular to the plate, the vertex of the cone being in the plane of the surface of the plate. The angle, θ, between the cone and plate surfaces is between 0.3-5°. There are a number of advantages in using small gaps such as the strain rate is uniform throughout the sample, the samples are retained better, the temperature rise is minimised and only small sample quantities are required. The parameters/ constants for the cone and plate system employed are given below.

Cone angle = 3° 58"
Cone diameter = 50.0 mm
Measurement system gap = 146 μm
Concentric Cylinders

The apparatus is shown in Figure 5.10(b). The inner cylinder of radius $R_1$ rotates inside a fixed outer cylinder of radius $R_2$. An approximation to a uniform shear rate is achieved by shearing a thin film of the liquid between the concentric cylinders. The inner cylinder can be continuously rotated (or oscillated) with the outer cylinder stationary and the resistance to rotation measured. The parameters for this arrangement are,

- $R_1 = 23.05$ mm
- $R_2 = 25$ mm
- Cylinder immersed height = 30.00 mm
- Measurement system gap = 4000 $\mu$m

![Figure 5.10](image-url) (a) cone and plate apparatus, (b) concentric cylinder arrangement.
5.3.2 Theory

(i) Flow Measurements

*flow* can be described by Figure 5.11. Imagine a cube of area, $A$, of the sample under consideration. There are several ways that a force, $F$, can be applied in order to deform this material but the one most usually considered in rheology is called the *shear force*. If the base is fixed and the sample is not resistant to the applied force, then the pattern of deformation will be as indicated by the dotted lines in the figure, and its extent $dx$ related to the magnitude $F$ and the sample's inherent ability to resist the applied force.

When the sample is an ideal elastic solid, the term used to relate the force per unit area (stress) and the deformation (strain) is called 'Young's Modulus'. Most colloidal systems exhibit behaviour that is viscoelastic i.e. with both viscous and elastic properties. The shear stress $\sigma = F/A$ (Nm$^{-2}$), the shear rate $\gamma = v/d$ (s$^{-1}$) and the viscosity $\eta = \sigma/\gamma$ (Nm$^{-2}$ s).

![Figure 5.11 Cube of area A, onto which a shear force F is applied](image)

If the shear stress is proportional to the shear rate, such that the viscosity is a constant, the sample is said to be *Newtonian*, and a graph of shear stress vs. shear rate is a straight line through the origin. However, some fluids encountered are non-Newtonian and this behaviour can manifest itself in a variety of ways e.g. some exhibit yield stresses, so that the applied stress has to exceed a certain value before any flow can occur, and the resulting flow can be linear (Bingham) or non-linear (plastic- e.g.
modelling clay). Fluids may be non-linear without exhibiting a yield stress and are shear thinning (pseudo-plastic) or shear thickening (dilatant). Shear thinning is characterised by a gradual decrease in the apparent viscosity with increasing shear, whilst when shear thickening occurs the viscosity increases with increasing rate of deformation. Figure 5.12 illustrates these types of non-Newtonian flow.

(ii) Creep experiments

*Creep* is defined as the slow deformation of a material. This is the simplest rheological experiment that can be performed. The technique applies a small stress (10-100 Pa) to the sample over a prolonged period and monitors the response of the strain, in order to reveal structural details that would otherwise be missed by continuous flow techniques. Figure 5.13 shows the application and removal of a small stress to three types of material, an elastic solid, a viscous liquid and a viscoelastic material. The creep curve for an ideal Hookean solid shows a total instantaneous response to the applied stress and no further flow. For the Newtonian fluid there is no instantaneous response but a continuous flow in response to the stress. The behaviour of the viscoelastic material is the most complex and can be represented by two architectural type models (see Figure 5.13),

(i) the behaviour of an ideal solid is analogous to that of a massless spring, and,
(ii) the behaviour of a Newtonian fluid can be represented by a dashpot whose rate of extension is proportional to the applied load.

![Diagram](image)

**Figure 5.13** Types of creep response showing (a) elastic deformation, (b) viscous flow and (c) viscoelastic response.

Creep curves were recorded for the 150, 250 and 300 TBN compounds in the stress range 0-10 Pa.

(iii) Oscillatory shear

An oscillation experiment is an example of a dynamic method and is concerned with the time response of the sample to a mechanical disturbance. One component of the rheometer undergoes a sinusoidal oscillation and the response of the other is monitored. The recorded stress curve at the inner cylinder or cone lags behind the strain curve imposed on the other cylinder or plate. Like the 'creep' technique, oscillatory analysis requires very little perturbation of the test material, but can provide a great deal of information on the equilibrium structure and stress relaxation mechanisms of the material. In oscillation, the stress varies as a sine wave. Varying the frequency, \( \omega \), of the applied wave at low amplitudes causes different structural elements of the sample to respond when their characteristic times are approximately
equal to $\omega^{-1}$. The technique excites a mechanical response from the system and because of this the technique is often termed 'mechanical spectroscopy'. In both electromagnetic radiation spectroscopy and this technique an applied and resultant signal are compared, but here the phase difference takes the place of absorption. The resultant strain wave can be out of phase from the input wave. A purely elastic response is characterised by a zero phase angle, whilst a phase angle of 90° is indicative of a purely viscous response. The response of a viscoelastic material lies in between these two extremes. (Figure 5.14(a)) Values of the complex modulus $G^*$ can be determined by this technique. (Figure 5.14(b)). $G'$ is called the storage modulus and measures the elastic response of the sample. The viscous response of the sample is characterised by the loss modulus, $G''$. The greater the phase angle the more fluid-like is the response.
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100% elastic

100% viscous

(a)

Figure 5.14 (a) Phase differences for viscous and elastic materials, (b) Determination of $G'$ and $G''$.

(b)

complex modulus $G^* = \frac{\text{shear stress}}{\text{shear strain}}$

storage modulus $G' = G^* \cos \delta$

loss modulus $G'' = G^* \sin \delta$
5.3.3 Results

Flow

Figure 5.15 shows the flow curves for the 150, 250 and 300 TBN samples. In each case the stress vs. shear rate curve is a straight line exhibiting a zero yield stress. This type of response is typical of a Newtonian fluid. Deviations from Newtonian flow are expected if the particles are aggregated. Dielectric measurements have indicated that these systems do contain quite large aggregates. The fact that the yield stress is so small (<1 Pa for each sample) indicates that the aggregation forces are weak and easily overcome by the applied shear stresses. The main cause of non-Newtonian flow is the breakdown of structure. Therefore if the liquid does have some structure it is very easily broken down by the shear flow. The viscosities obtained were 12.80, 81.53 and 254.60 Pa.s for the 150, 250 and 300 samples respectively.

Creep

The creep curves for the 150, 250 and 300 TBN neat samples with an applied stress of 50 Pa are shown in Figure 5.16. As the stress is applied there is no instantaneous response, but a continuous flow in response to the stress. However, when the stress is removed (at t=600s) there is no tendency for the material to relax back to its original state. This type of response is typical of a purely viscous (Newtonian) fluid. The calculated viscosities for the 150, 250 and 300 TBN samples are 14.99, 81.90 and 251 Pa.s respectively.
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Oscillation

The response of the system to a range of frequencies is illustrated in Figure 5.17. By measuring the visco-elastic parameters $G'$ and $G''$ and the viscosity, $\eta$, as a function of frequency more detailed information about the dynamical processes in the sample can be obtained. Figure 5.17(a) shows the trace for the 150 TBN sample in the frequency range 1-10 Hz. The viscosity remains constant at a value of approximately 15.05 Pa s throughout this range. The phase difference, $\delta$, responds in a similar way with an average value of 89.80°. Both the storage modulus and the loss modulus increase with frequency, with the loss modulus being greater in value than the storage modulus. This is typical liquid-like behaviour. If the storage modulus was greater in value than the loss modulus this would be an indication of solid-like (elastic) behaviour. All liquids are viscoelastic to some extent. A change is observed from predominantly liquid-like behaviour ($G''>G'$) at low frequency and low concentration, to a solid-like behaviour ($G'>G''$) at high frequency and high concentration followed by a levelling out to a constant value in the high frequency limit (>100 Hz). Figures 5.17(b) and 5.17(c) show the 250 and 300 TBN graphs respectively. Once again the same behaviour is shown as for the 150 TBN material. The viscosities calculated for 250 and 300 TBN compounds are given in Table 5.6.

The basic model for a viscoelastic liquid was derived by Maxwell. He assumed that stress relaxation in a liquid took the form of a single exponential decay function, $G_\infty \exp(-t/\tau)$, where $G_\infty$ is the infinite frequency shear rigidity modulus, and $\tau$ is the Maxwell relaxation time. $\tau = \eta_0/G_\infty$ where $\eta_0$ is the Newtonian viscosity (the viscosity in the limit of zero shear rate or zero frequency). For this model fluid we have,

$$G'(\omega) = \frac{G_\infty (\omega \tau)^2}{1 + (\omega \tau)^2}$$  \hspace{1cm} \text{eqn. 5-11}$$

and
\[ G''''(\omega) = \frac{G_n(\omega \tau)}{1 + (\omega \tau)^2} \]  

eqn. 5-12

Therefore in this model, \( G'(\omega)/G''(\omega) = \omega \tau \) and by plotting \( ln(G'/G'') \) against \( ln\omega \), a straight line of intercept \( hrt \) results, thus enabling the calculation of the stress relaxation time, \( \tau \). Table 5.6 shows the results for the different TBN samples. As can be seen the 150 TBN material has the shortest relaxation time, whilst the 300 TBN has the longest relaxation time. This is reasonable as the 300 TBN has a greater percentage of solids in it than either the 250 or 150 TBN. The relaxation times \( (\tau_c) \) from the dielectric measurements are similar to those obtained using this technique indicating that the stress relaxation time is associated with a mean "collisional" time between the aggregates.

Table 5.6  The stress relaxation times for solutions of the neat detergent samples measured by oscillatory shear rheometry.

<table>
<thead>
<tr>
<th>TBN</th>
<th>( \tau /10^{-3}/s )</th>
<th>Newtonian Viscosity /Pa.s</th>
<th>Newtonian Viscosity (Ostwald) /Pa.s</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>1.294</td>
<td>14.94</td>
<td>0.0616</td>
</tr>
<tr>
<td>250</td>
<td>3.70</td>
<td>81.50</td>
<td>0.2374</td>
</tr>
<tr>
<td>300</td>
<td>8.65</td>
<td>254.60</td>
<td>0.4773</td>
</tr>
</tbody>
</table>

To conclude, it would appear that the neat additives are essentially classical Newtonian liquids under continuous shear. Any aggregates in the solution clearly break up very easily and would therefore appear to have little consequence for the performance of the additives in their working states. The visco elastic relaxation time of the liquids is measurable, and is of the same order of magnitude as the dielectric relaxation time (cf. Tables 5.1-5.5). This indicates that diffusional processes between the colloidal particles are responsible for stress relaxation in these systems.
Figure 5.15 Flow results for (a) 150 TBN, (b) 250 TBN and (c) 300 TBN neat additives.
Figure 5.16 Creep results for (a) 150 TBN, (b) 250 TBN and (c) 300 TBN neat additives.
Figure 5.17 Oscillatory curves for (a) 150 TBN, (b) 250 TBN and (c) 300 TBN neat additives in the range 0-10 Pa.
5.4. Dynamic Light Scattering

When light impinges on matter, the electric field of the light induces an oscillating polarisation of the electrons in the molecules. These molecules then serve as secondary sources of light which subsequently emit light. The frequency shifts, the angular distribution, the polarisation and the intensity of the scattered light are determined by the size, shape and molecular interactions in the scattering material. Therefore light scattering enables the determination of these molecular characteristics. If a laser is used, the light is coherent and interference patterns are produced by an array of particles. If the particles are stationary, a scattering pattern is seen. If the particles are in continuous motion (colloidal dispersions) the pattern of spots changes intensity continuously leading to a mobile speckle pattern, and the light appears to 'twinkle', the time dependence of which is related to the motion of the particles. In dynamic light scattering (DLS), the time dependent intensity is measured by a photon correlator, which enables the correlation in time between the fluctuations in light intensity to be computed. The result is a correlation function which represents the relation between the average intensity at a time \( (t + \tau) \) and that at time \( t \). When \( \tau \) is large the intensity of the scattered light \( I(t) \) and \( I(t + \tau) \) are independent of each other, and the correlation function tends to zero. This function is a measure of the probability of a particle moving a given distance in time \( \tau \). If the particles are spherical, the correlation function, \( g(\tau) \) can be expressed as an exponential function,

\[
g(\tau) = A < I(t + \tau)I(t)> = \exp(-\tau/\tau_c)
\]

where \( A \) is a constant, \(<I(t+\tau)I(t)>\) denotes an average over time, \( t \), and \( \tau_c \) is related to the diffusion coefficient, \( D \) by,

\[
\tau_c = 1 / DQ^2
\]
where $Q$ is the wave vector \( Q = (4\pi/\lambda) \sin(\theta/2) \), $\theta$ the scattering angle and $\lambda$ the wavelength of the light. A plot of $\ln g(\tau)$ vs. $\tau$ yields $\tau_c$. The hydrodynamic radius, $a$ of the particles can be determined using the Stokes-Einstein equation,

$$a = \frac{kT}{6\pi\eta}Q^2\tau_c$$

eqn. 5-15

The assumption here is that the scattering particles are all the same size and shape i.e. monodisperse. The analysis becomes more complicated for a polydisperse system, as the correlation function will have components from the different species.

**5.4.1 Results**

A sample was submitted to the 'Polymer & Colloids' group at Cambridge University for analysis. The 250 TBN and 300 TBN samples were prepared as 1% (by weight) concentrations in toluene and the results are discussed below.

**250 TBN**

Figure 5.18(a) shows the particle size distribution against the intensity distribution for the 250 TBN particles. It is apparent that the particles are quite large with the size covering a wide range (200-900 nm). The average hydrodynamic radius of these particles is 250 nm assuming a monomodal size distribution using a cumulants fit procedure (although it is evident that the distribution is bimodal with a large spread of particle size). The average particle size obtained using this procedure is rather large but consistent with the results obtained using the dielectric technique. The effective aggregate size is larger using DLS than from the dielectric measurements.
Figure 5.18(b) shows the particle size distribution for the 300 TBN particles, with an average hydrodynamic radius of 180 nm. As for the 250 TBN, the particle sizes obtained are on the large side.

5.5 Summary

The dielectric spectroscopy and dynamic light scattering reported in this chapter have provided evidence for a substantial level of aggregation of the detergent micelles in dilute solution. However it would appear that these aggregates have a negligible effect on the rheology in the neat samples and probably therefore in the diluted state. This could be because the aggregates are weakly held together and break up readily under applied stress. The consequences of aggregation are probably insignificant for the rheological behaviour of these additives in the working engine, although they could have some effect on their reactivity
Figure 5.18 Light scattering results for (a) 250 TBN and (b) 300 TBN adducts in toluene.
Chapter 6. Conclusions & Future Work
6.1 Conclusions

In order to build up a picture of these overbased detergents I found it essential to apply a range of experimental and theoretical techniques which complemented one another. This was certainly a multidisciplinary project.

6.1.1 Chemical nature

A series of model overbased detergents were made with carbonate to phenate ratios of 1:1, 1.67:1 and 2:1 for the 150, 250 and 300 TBN samples respectively. These were analysed using several techniques (UV, FTIR, NMR and TLC), and the chemical species were identified. I found UV absorption a very useful technique for compositional analysis. The UV spectra gave clear evidence of the presence of the phenate anion in the detergent sample. *Ab initio* quantum mechanical calculations supported this conclusion. FTIR spectra of the alkyl phenol and the additive were compared. The most striking feature between the two is the disappearance of the peaks at 3339 and 1241 cm\(^{-1}\) in the spectrum of the additive, again indicating the absence of the phenol in the additive. A peak at 862 cm\(^{-1}\) in the spectrum of the additive confirmed the presence of carbonate in the core of the additive. There was no evidence for the presence of unreacted Ca(OH)\(_2\). The reaction appears to have gone 'cleanly' to the desired products with no noticeable impurities. Clearly the established synthesis procedure is quite well optimised.

\(^1\)H NMR spectrum of the alkyl phenol gives a well resolved spectrum showing aliphatic protons, phenolic protons and aromatic protons in the ratio 1:4:25, indicating a C\(_{12}\) chained structure. The fact that there are several different types of aliphatic protons suggests a branched chain. The corresponding spectrum of the additive was poorly resolved especially in the region of the aromatic protons. \(^{13}\)C solid state NMR of the extracted adduct resolved the aliphatic and aromatic carbons, as well as
providing evidence for the presence of carbonate in the sample. The broadness of these peaks suggests a disordered sample which may be evidence for an amorphous core, as suggested by previous EXAFS studies on overbased sulphonate systems.

6.1.2 Physical Nature

The Langmuir trough experiments gave a great deal of useful information about the size of the detergent particles, how they vary with TBN, and the interaction forces between them. Particle diameters of 2.49, 2.95 and 3.15 nm were obtained for the 150, 250 and 300 TBN respectively, which when plotted gave a linear relationship and enabled a shell thickness of 1.90 nm to be determined. Once the core diameters were known, the numbers of the calcium carbonate and calcium phenate could be calculated, making use of the previous compositional analysis. The interaction potential between the particles determined from the Langmuir trough technique, showed that the chains could be squashed by about 15% but otherwise the interactions were rather hard.

Further information on the interfacial nature of the particles was gained by measurement of the contact angle. The lower the TBN, the more hydrophobic was the sample, which is reasonable as there is less inorganic content in the lower 150 TBN than there is in the 250 or 300 TBN. The surface tension measurements contradicted this to some extent. As before the 150 TBN appeared the most hydrophobic, but the 300 TBN was more hydrophobic than the 250 TBN. The discrepancy indicates that the conformational state of these micelles could be different on a water surface as compared to in a hydrophobic solvent. One implication of this is that the 300 TBN particles are able to "protect" the core better than the 250 TBN in a hydrophobic solvent. (They are able to do this in a hydrophobic medium but not on water, perhaps, where the surfactant chains are likely to be more bundled together).
6.1.3 Computer Simulations

The simulations gave much useful atomistic detail about the individual overbased micelle particles. The phenate molecule would appear to be a rather rigid structure, by virtue of the sulphur bridge. As the alkyl chain length increases, the strain energy increases, so that above about C\textsubscript{8} the two alkyl chains cease to be parallel but extend in opposite directions. This could have implications for optimum chain lengths required for stability of the micelles. The sulphonates are single alkyl chain systems, which are not chemically joined together, so this cross-over feature does not apply to these detergent systems.

When phenate surfactants were introduced together with calcium carbonate molecules, an inverse micellar structure was naturally formed, with the carbonate at the centre and the surfactants in a shell around this core. These structures differed quite a lot with TBN: the 150 was wedge shaped, the 250 was disc-shaped and the 300 TBN was more ellipsoidal. The structure of these overbased micellar systems was stable at elevated temperature (650 K), and is probably due to the strong coulombic interactions in the core between the calcium carbonate molecules, suggesting that they would behave in a similar way in a working engine. This is in marked contrast to water containing systems, where there are large fluctuations in the shape of the micelles. The micelle is swelled out to a limited extent in the presence of a generic hydrocarbon solvent. The sulphonate systems were quite different being essentially spherical at all TBNs in excess of 150.

The inclusion of a co-surfactant in the 250 TBN phenate micelle system resulted in the size of the core increasing as they wedged between the surfactant molecules in an otherwise crowded equatorial shell. It would appear that the geometry of the
individual surfactant molecule and any co-surfactant can have a strong influence on the shape and possibly maximum size of the micelle.

6.1.4 Bulk behaviour

The dielectric spectroscopic measurements produced some interesting results. It is apparent from this technique that these particles do have a tendency to aggregate, with the aggregate size being relatively large, containing many thousands of micelle units. The aggregate size is affected by a number of factors, although there is very little variation in size with TBN. The aggregate size increases with concentration. This effect was relatively insensitive to the chemical nature of the solvent system, provided it was hydrophobic. The neat detergent samples diluted in toluene showed similar results i.e. the aggregate size was still large but there was not the same concentration dependence as for the extracted adduct.

The rheology of the neat samples of 150, 250 and 300 TBN detergents showed Newtonian behaviour with unmeasurable yield stresses. This indicates that any aggregates that persist to high volume fractions are only very weakly held together and are broken up on the application of the kind of stresses also likely to be found in an engine. Dynamic light scattering also gave evidence for a large agglomeration of the detergent micelles, although they were quite a lot bigger than those indicated by the dielectric spectroscopy. The significance of the aggregation is not really known yet but there could be some consequences for the rate at which these detergents react in the engine.
6.2 Future Work

The work carried out brought to the surface a number of other pieces of investigation that I think would be interesting to carry out. I list them in the same order as before.

6.2.1 Chemical and Physical characterisation

The analytical techniques used to characterise the overbased detergents are now well developed and can adequately determine their chemical composition. In contrast, the physical state of the system is still uncertain in some respects. For example, the shape of the micelles could not be determined in the present work. Also I could not determine if a mixture of different micelle sizes are produced in the synthesis. It seems surprising that the synthesis procedure should produce particles of the same composition and size. Small angle neutron scattering could possibly answer these questions. The core holds the particle together, but its structure (certainly for the phenates) is still largely unknown. EXAFS would be a potentially useful technique to study the state of the core, and could determine where the ions of CaCO$_3$ are with respect to the head groups. EXAFS could also yield information as to whether the charge distribution is uniform throughout the carbonate core.

The physical state of the micelles in the engine is still uncertain. The dielectric and light scattering showed that large aggregates formed, but lack of time prevented me from exploring these aspects in greater detail. Other techniques such as Small Angle X-ray Scattering (SAXS) may be useful in this respect, as would electrophoresis in determining whether the particles are charged.
6.2.2 Computer simulation

The simulations proved very informative, and have raised many interesting questions that could be investigated by further work of this nature. Some ideas I have are itemised below.

(1) The current simulations have shown that the surfactant geometry has a pronounced effect on the structure of the inverse micelles. As salicylates are becoming increasingly popular it would be interesting to simulate these detergent types. Salicylates are typically long single straight chain molecules and are more chemically similar to the sulphonates than to the phenates. On the evidence presented in this thesis, one might expect them to form spherical micellar structures (cf. sulphonates) in preference to the more disc-shaped structures formed by the phenates. Mixtures of different detergent types are believed to have a synergistic effect on the performance of the detergent, and most commercial lubricants contain more than one type of detergent. Simulations could be performed to investigate this effect.

(2) This simulation work has shown that the inclusion of solvent has an effect on the overall shape of the clusters. A generic hydrocarbon solvent (i.e. hexane) was used in the simulations presented in this thesis. Lack of time prevented me from carrying out more realistic representations of the solvent which I recommend for future work. The interaction between the particles is also dependent on the choice of solvent (dielectric results). In reality, base oils are not purely aliphatic or aromatic but generally a poorly defined mixture containing both. It would be interesting to see the effect on the structure of the micelles of the inclusion of some aromatic solvent (e.g. toluene) as well as the hexane to provide a much more realistic model for the solvent. Different methods for introducing the solvent should be
considered. The solvent in this work was introduced after the micelle had been assembled. When these detergents are synthesised, the solvent is included from the start. It may be possible to perform a simulation where the solvent molecules are included from the beginning. At this time however, computer power limitations prevented this from being done:

(3) It has been shown that for systems of aqueous core inverse micelles formed by AOT, the stabilising metal cations have an important effect on their shape. Eastoe et al showed that the shape of AOT based water-in-oil microemulsions is changed from a sphere to another non-spherical shape by changing the cation from $\text{Na}^+$ to a doubly charged cation such as $\text{Ca}^{2+}$, $\text{Mg}^{2+}$.\textsuperscript{100} There could be parallel effects for the present systems of overbased detergents. In aqueous systems of SDS (Sodium dodecyl sulphate) a similar effect has been observed. For example, the addition of a salt promotes growth of the spherical micelles into rod shaped aggregates.\textsuperscript{101}

(4) It would be interesting to carry out simulations of several of these micelles in a model solvent to learn more about how they interact, and therefore if the mechanism of aggregation can be better understood. These simulations would prove to be expensive computationally and this might have to wait for the next generation of workstations.

(5) The obvious extension of this work is to investigate the interactions between different additive types (e.g. dispersants, anti-wear additives), and what effect this has on the structure of the detergents. I consider this to be very important as this is ultimately what governs the operating mechanism within the fully formulated lubricant in the engine. This again may be beyond current computational powers. A parallel experimental programme of work would need to be carried out here.

(6) Chemical reactivity is another related topic I did not have time to explore by experiment but would still be interesting to look at in future work.
References
References


[28] Private communication with Mr. C. Cane, ADIBIS, Hull.

[29] GAUSSIAN92, M. J. Frisch, P. M. W. Gill, M. W. Wong, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, B. G. Johnson, C. Gonzalez, D. J. Defrees, D. J. Fox, E. S. Replogle, R. Gomperts, J. L. Andres, R. L. Martin, J. Baker, J. J. P. Stewart & J. A. Pople, Gaussian Inc., Pittsburgh PA, USA.


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