SHEAR-INDUCED STRUCTURES
IN A COMMERCIAL SURFACTANT-BASED SYSTEM

Marianne Su-Ling Liaw

Jesus College

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The work presented in this dissertation was carried out in the Department of Chemical Engineering, University of Cambridge, between October 2000 and October 2003. It is the original work of the author and includes nothing which is the outcome of work done in collaboration, except where specifically indicated in the text. No part of this dissertation has or is currently being submitted for any degree, diploma or other qualification at this or any other university.

This dissertation is approximately 48,000 words in length (including appendices, bibliography, tables and equations) and contains 58 figures.

Marianne Su-Ling Liaw

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LAS (Linear Alkylbenzene Sulfonate) is a commercially important surfactant; its global consumption is worth billions of pounds every year. Despite this, its behaviour is poorly understood, particularly during industrial processes such as those used in the detergent industry for the manufacture of compact detergent powders. Such powders are successfully manufactured by the surfactant agglomeration process. Prior to the agglomeration stage, a paste-structuring process is used to modify the properties of the concentrated paste-like surfactant that is part of the detergent formulation. This ensures that the surfactant paste is of a suitable consistency for the agglomeration process and to enable high levels of surfactant to be incorporated into the detergent granules. Surfactant pastes with successfully modified properties are deemed ‘structured’. When LAS-based compact detergent powders are produced, high-active LAS (a highly concentrated surfactant system of ca. 80 wt. % LAS molecules in water) is used and paste structuring is conducted in a twin-screw extruder where the structuring agent, sodium disilicate, is added.

The aim of this work has been to contribute to the scientific understanding of paste-structuring with high-active LAS. The approach has focussed on studying the effect of added salts on the microstructure and rheological behaviour of high-active LAS with shear\(^1\) and relating this to paste-structuring. The results show that industrially structured high-active LAS possesses a packed MLV (Multi-Lamellar Vesicle) microstructure, and that during the paste-structuring process a transition from planar lamellae to MLVs occurs with the application of shear. A range of MLV-inducing salts has been identified and the effects of temperature, salt concentration and shear duration have been studied. The stability of MLVs has also been investigated. The tightly-packed MLV microstructures produced by different salts were found to vary in firmness and to be related to the size and size distribution of MLVs within the sheared pastes. In addition, salts without an effect on the behaviour of high-active LAS under shear have been identified as well as salts that promote shear-induced phase separation and the formation of large ‘worm-like’ structures that have not previously been reported in the literature.

\(^1\) Steady shear conditions; apparent wall shear rate of 1,100 s\(^{-1}\)
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\( a \)  Perpendicular orientation state (\( n \parallel z \))
\( a_o \)  Molecular area requirement of surfactant hydrophilic group
\( b \)  Transverse orientation state (\( n \parallel v \))
\( c \)  Parallel orientation state (\( n \parallel \nabla v \))
\( d \)  Fundamental repeat distance, inter-lamellar distance (Å)
\( D \)  Internal diameter of capillary (m)
\( D_b \)  Internal diameter of MPR barrel (m)
\( f_j \)  Individual structure factor
\( F \)  Total scattering factor (or structure factor)
\( F \)  Tangential force
\( G \)  Shear modulus (Pa)
\( h \)  Height of an object, separation between two flat parallel plates (m)
\( I \)  Scattered X-ray intensity (arbitrary units)
\( I_0 \)  Incident X-ray intensity (arbitrary units)
\( I_t \)  Transmitted X-ray intensity (arbitrary units)
\( L \)  Length of an object (m)
\( l_c \)  Effective length of alkyl chain
\( n \)  Order of diffracted beam, integer number of -(CH\(_2\)) groups
\( n \)  Bilayer normal unit vector
\( N \)  Number of scattering centres in a sample
\( p \)  Packing parameter
\( P_t \)  Top transducer pressure (bar)
\( P_b \)  Bottom transducer pressure (bar)
\( Q \)  Volumetric flowrate (m\(^3\) s\(^{-1}\))
\( r \)  Real-space vector with the origin at a scattering centre
\( s \)  Scattering vector
\( s \)  Shape factor
\( S \)  Scattered X-ray beam unit vector
\( S_0 \)  Incident X-ray beam unit vector
\( v \)  Flow vector
\( v \)  volume
\( v_p \)  Piston speed (mm s\(^{-1}\))
\( \nabla v \)  Shear gradient
\( V \)  Total X-ray-irradiated volume of a sample
\( x \)  X-ray path-length (sample thickness) (cm)
\( x \)  x-axis
\( X_b \)  Position of MPR bottom transducer
\( y \)  y-axis
\( z \)  z-axis
Symbols

\( \gamma \) \hspace{1cm} \text{Shear strain}
\( \dot{\gamma} \) \hspace{1cm} \text{Shear rate, apparent shear rate (s}^{-1}\text{)}
\( \dot{\gamma}_w \) \hspace{1cm} \text{Wall shear rate, apparent wall shear rate (s}^{-1}\text{)}
\( \delta \) \hspace{1cm} \text{Wave path difference (m)}
\( \eta \) \hspace{1cm} \text{Viscosity, apparent viscosity (Pa s)}
\( \theta \) \hspace{1cm} \text{Scattering angle (º)}
\( \lambda \) \hspace{1cm} \text{Wavelength of incident X-ray beam (Å)}
\( \mu \) \hspace{1cm} \text{Total linear absorption coefficient (cm}^{-1}\text{)}
\( \mu_m \) \hspace{1cm} \text{Mass absorption coefficient (cm}^{2}\text{g}^{-1}\text{)}
\( \nu \) \hspace{1cm} \text{Molecular hydrophobic group volume}
\( \rho \) \hspace{1cm} \text{Electron density}
\( \tau \) \hspace{1cm} \text{Shear stress (Pa)}
\( \tau_w \) \hspace{1cm} \text{Wall shear stress (Pa)}
\( \chi \) \hspace{1cm} \text{Azimuthal angle (º)}
\( \Delta P \) \hspace{1cm} \text{Pressure difference (bar)}
\( \Delta P_p \) \hspace{1cm} \text{Pseudo-steady pressure difference (bar)}
\( \Delta L \) \hspace{1cm} \text{Change in length due to shear (m)}

Subscripts

\( j \) \hspace{1cm} \text{Refers to the } j \text{th number of scattering centres}
\( x \) \hspace{1cm} \text{Refers to the } x \text{ direction}
\( yx \) \hspace{1cm} \text{Refers to the plane normal to } y \text{ and the } x \text{ direction}

Acronyms

AOT \hspace{1cm} \text{Aerosol-OT (sodium bis-(2-ethylhexyl) sulfosuccinate)}
C \hspace{1cm} \text{Carbon atom}
(C_{6}H_{5}O_{7})^{3-} \hspace{1cm} \text{Citrate ion}
Cl^{-} \hspace{1cm} \text{Chloride ion}
Cryo-SEM \hspace{1cm} \text{Cryogenic scanning electron microscope}
H \hspace{1cm} \text{Hydrogen atom}
H_{1} \hspace{1cm} \text{Normal hexagonal liquid crystal phase}
HLAS \hspace{1cm} \text{Linear alkylbenzene sulfonic acid}
K^{+} \hspace{1cm} \text{Potassium ion}
L_{1} \hspace{1cm} \text{Normal micellar phase}
L_{\alpha} \hspace{1cm} \text{Lamellar liquid crystal phase (idealised form)}
LAB \hspace{1cm} \text{Linear alkylbenzene}
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAS</td>
<td>Linear alkylbenzene sulfonate</td>
</tr>
<tr>
<td>MLV</td>
<td>Multi-lamellar vesicle</td>
</tr>
<tr>
<td>MPR</td>
<td>Multi-Pass Rheometer</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen atom</td>
</tr>
<tr>
<td>Rheo-NMR</td>
<td>Rheological Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Sodium ion</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>Ammonium ion</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>Nitrate ion</td>
</tr>
<tr>
<td>O</td>
<td>Oxygen atom</td>
</tr>
<tr>
<td>OH⁻</td>
<td>Hydroxyl ion</td>
</tr>
<tr>
<td>P</td>
<td>Phosphorous atom</td>
</tr>
<tr>
<td>PID</td>
<td>Proportional integral derivative (circuit which controls piston position in the MPR)</td>
</tr>
<tr>
<td>S</td>
<td>Sulfate atom</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon atom</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>Sulfate ion</td>
</tr>
<tr>
<td>TMA</td>
<td>Tetramethyl-ammonium</td>
</tr>
<tr>
<td>TDMAO</td>
<td>Tetradecyldimethylamine oxide</td>
</tr>
<tr>
<td>TTABr</td>
<td>Tetradecyltrimethylammonium bromide</td>
</tr>
<tr>
<td>ULV</td>
<td>Uni-lamellar vesicle</td>
</tr>
<tr>
<td>WAXS</td>
<td>Wide-angle X-ray scattering</td>
</tr>
</tbody>
</table>
1.1 A Brief History of Soaps and Detergents

The history of soaps and detergents dates back 2000-3000 years (Woollatt, 1985). The Romans and other civilizations around the Mediterranean Sea are known to be some of the earliest users of soaps. In the saponification or soap-making process, alkalis and fats/oils are required. Early examples of sources of crude alkaline carbonates include barilla (obtained from the ash of seaweeds), wood ash and stale urine. The fats tended to come from domestic animals and olive oil was sometimes used. As the chemical industry developed, alkalis such as sodium carbonate and sodium hydroxide replaced the early alkali sources and, in England, local tallow was the major fat used.

Synthetic ‘non-soapy’ detergents were developed during the first and second world wars to replace the neutralised fatty acid soaps that were used in laundry products. These early detergents were developed in response to the scarcity of animal fats and were based instead on petroleum. By the mid-1950s products based on non-soapy detergents had obtained a major share of the market in many developed countries (Woollatt, 1985).

Detergents are cleaning products formulated with several components; of these, the surfactant component has a vital role (Clint, 1992). Surfactants are important as they reduce the surface tension of water, allowing the detergent to remove and solubilise fatty deposits from the soiled substrate (Herman de Groot, et al., 1995). The surfactants used in the early synthetic detergents were the highly-branched alkylbenzene sulfonates (ABS). However, due to the non-biodegradable nature of ABS, these surfactants were replaced in the mid-1960s with the more biodegradable linear alkylbenzene sulfonates (LAS¹), (Showell, 1998).

¹ In this document, LAS refers to the linear alkylbenzene sulfonate salts produced from commercial mixtures obtained from petroleum.
1.2 LAS in the Surfactant Industry

The global surfactant industry is a multi-billion pound business and is one of the largest chemical process industries in the world (Kirk and Othmer, 1991). Every year, several million tonnes of synthetic surfactants are used in a variety of markets ranging from personal care products to explosives. However, the use of surfactants in household detergents is of greatest importance commercially; as it accounts for approximately 40% of the overall surfactant market value (Hargreaves, 2003).

In 1998, the annual global consumption of the surfactant LAS was over 800,000 tonnes, worth around £2 billion; in future years, this level of demand is projected to continue. Most of the LAS is used in formulated household detergent products, particularly in laundry detergent powders where almost half of the LAS produced is consumed (Modler, et al., 1999). The success of LAS in these products has been due to its favourable detergency and foaming properties, low cost, easy processing, versatility of application and biodegradability (Matheson, 1996). Despite the immense industrial importance of LAS, on a fundamental level there is surprisingly little phase information available (Laughlin, 1994) and published data on LAS is also limited. The industrial approach to the improvement and development of processes involving LAS has therefore relied largely on a trial-and-error approach (McKeown, 2001), leaving scope for systematic scientific exploration of the industrial materials and processes.

1.3 Laundry Detergent Powders: Regular versus Compact Products

In the manufacture of detergent powders, Herman de Groot et al. (1995) identify the major challenge as the need to convert an arbitrary mixture of liquids, and pulverized powder components into a homogeneous, free-flowing, well-dissolving granular product. The standard components of detergent powders are listed in Table 1.1, along with their function. Traditionally, the detergent industry has produced detergent powders by spray-drying the formulation mixture, resulting in ‘regular’ detergent powders with bulk densities of about 200
to 500 g/L (Showell, 1998). However with the introduction of a compact high-
density powder in Japan during the late 1980s, a marked shift from regular to
compact detergent powders occurred. Today, concentrated compact detergent
powders, with bulk densities typically of 600 to 900 g/L, have largely replaced
the traditional low-density powder products in the United States, Europe and
Japan and are spreading to the other parts of the world (Showell, 1998).

In comparison to regular detergent powders, compact powders require less
packaging per product, and are therefore more convenient for both consumers and
retailers. This is because compact detergents are designed to minimise the
laundering dosage volume by increasing the particle density of the powder
granules (thereby decreasing the volume of air in the product) and maximising
the surfactant content (Raney, 1998). The formulation of compact powdered
detergents differs from the regular low-density powder products in that minimal
amounts of fillers are used, with generally more surfactant present.

There are also geographical variations in both compact and regular detergent
powder formulations, due to differences in regulations, laundering practices and
water quality (Herman de Groot et al., 1995). Table 1.2 compares typical
formulations for European and Japanese regular and compact detergent powder
products.

Spray-drying has long been the preferred method for manufacturing regular low-
density detergent products. The initial compact powders available on the market
were manufactured using existing spray-drying technology with modifications to
the product formulation and operating conditions, and post-treatment operations
(e.g. coating) (Capeci and Welch, 1998). However, the demands for greater
cleaning action and even smaller dosage volumes have led to the development of
innovative processing technologies for the manufacture of compact powders.
The early 1990s have seen the emergence of processes, such as post-tower
densification and compaction, used in conjunction with spray-drying to increase
the bulk density of powders (Capeci and Welch, 1998). Although spray-drying is
an established process, there are associated disadvantages: heat-sensitive
materials may degrade during processing, while the energy-intensive
requirements for operating the plant can be costly and detrimental to the
environment. In the late 1990s, these factors have seen many major detergent
manufacturers move to processing routes for compact powders, such as agglomeration, that are not reliant on spray-drying methods (Capeci and Welch, 1998).

1.4 Surfactant Agglomeration for Producing LAS-Based Compact Detergent Powders

1.4.1 Overall Process Description

Surfactant agglomeration is a process in which high-density detergent powder granules are created from a formulated mixture of primary powders and liquids using a highly concentrated (‘high-active’) surfactant paste as a ‘binder’, to bind the components together. The key advantages of this process are that the desired proportion of surfactant and builder can be incorporated into the granules and that there is flexibility for adding a variety of surfactants, builders and other functional ingredients to the granules (Capeci and Welch, 1998). One route for the production of LAS-based compact powders used by major detergent manufacturers is shown schematically in Figure 1.1. The main stages in this process are: (1) paste-structuring, (2) agglomeration and (3) conditioning & post-addition.

In the paste-structuring stage, high-active LAS paste$^2$ is used, often with other surfactants. The surfactants are fed through a twin-screw extruder at 60 °C with colloidal sodium disilicate powder and extruded through a die plate at pressures of up to 30 bar, forming an extrudate. The extrudate then undergoes a two-part agglomeration stage. In the first part, a high-speed mixer is used to rapidly cut up and distribute the extrudate amongst solid builders, initiating agglomeration. The second part involves a low-speed mixer, where the agglomerates or granules are built up to the required size. In the conditioning & post-addition stage, the wet granules are sieved and those that are not of the desired size are removed and sent back to the agglomeration stage of the process. The conditioning of the granules occurs as they are dried and subsequently cooled in a fluidised bed. During the post-addition step, the conditioned granules are dosed with brand-
specific solid additives (e.g. sodium carbonate and enzymes) and these are then mixed in a drum, where small amounts of liquid additives (such as perfumes and non-ionic surfactants) are sprayed on.

1.4.2 Industrial ‘Structuring’ of LAS Paste

In the surfactant agglomeration process, paste-structuring is extremely important. Its purpose is to alter the rheological properties of the surfactant paste, as this enables agglomeration to occur and also determines the surfactant loading capacity of the high-density granules (Capeci and Welch, 1998). ‘Paste-structuring’ is a general term used in the detergent industry to describe any process that makes a paste-like surfactant-based system more ‘solid-like’. Such pastes are considered to be ‘structured’ (McKeown, 2001).

In the paste-structuring process described in Section 1.4.1, the high-active LAS paste typically contains up to ca. 80 %

3 LAS molecules (‘active matter’) in water. Prior to structuring, at the process temperature of ca. 60 °C, high-active LAS appears as a highly viscous paste. Due to its ‘sticky’ qualities it is an effective binder, however its consistency is not suitable for agglomeration as it is not sufficiently ‘solid-like’ to be cut up and distributed in the high-speed mixer. When a small amount of structuring agent, such as colloidal sodium disilicate, is mixed into LAS paste at 60 °C as it undergoes mechanical deformation (in this case, via a twin-screw extruder), the resultant paste extrudate is less sticky, firmer, more solid-like and structured. This modification of LAS paste properties allows the paste to be cut up and dispersed in the high-speed mixer for agglomeration. The structured paste is also understood to act as a relatively less effective binder, enabling greater amounts of surfactant to be incorporated in each granule. Currently, the maximum level of LAS in typical compact products is 9.5 % (McKeown, 2001), and higher levels are desirable for more compact products.

Despite the importance of the paste-structuring process, it is poorly understood.

2 ‘High-active LAS’, ‘high-active LAS paste’ and ‘LAS paste’ are all terms referring to a commercial surfactant system used for agglomeration, consisting of ca. 80 wt.% LAS molecules in water; it has the consistency of a paste-like material.

3 Unless specified, percentages are given on a weight by weight basis.
Until recently, there was no explanation for the ability of LAS paste to convert into structured paste in the absence of structuring agents; during the transportation of LAS paste through factory pipes, paste-structuring of high-active LAS paste has been known to occur, causing blockages. In a study on the processing behaviour of high-active LAS paste without the use of structuring agents, the process temperature, pressure and level of mechanical deformation (apparent wall shear rate) were identified as key factors in determining whether structuring of the paste would occur (McKeown, 2001). The results also showed that the change in material properties of these structured pastes was due to a modified microstructural arrangement of molecules within the pastes. There are however, other conditions where the addition of structuring agents is required for structuring of LAS paste to take place. Industrial data indicate that various additives (e.g. sodium hydroxide, potassium hydroxide, sodium chloride) can be used as paste-structuring agents, in solid or liquid form, depending on their chemical properties (Auoad, et al., 1997). However, the mechanisms by which the structuring agents cause LAS paste to structure remain unknown.

1.5 The Present Work

1.5.1 Scope
From an industrial perspective, there is great value in understanding how to manipulate the material properties of LAS paste by paste-structuring; the importance of the paste-structuring process in the production of compact detergent powders and in the development of higher-active compact detergent powder products has been discussed. The present investigation extends the work on paste-structuring by McKeown (2001) on a commercial high-active LAS-based paste system. In that study, it was recognised that in order to investigate the mechanisms present in the industrial paste-structuring process a reproducible scientific investigation was required. Thus, the processing system was simplified from an industrial-scale twin-screw extruder to a novel laboratory-scale extruder (the Cambridge Multi-Pass Rheometer or MPR) where well-defined shear could be applied and the processing behaviour of high-active LAS paste was studied alone, in the absence of structuring additives. The combined engineering and
materials science approach that was taken during the study varied certain process parameters (temperature, apparent shear rate and pressure) and used microstructural data to explain the resultant processing behaviour and material properties of the LAS paste.

The purpose of the current investigation is to study the effect of various additives on the microstructure and processing behaviour of high-active LAS paste, using a similar approach to that used by McKeown (2001). Of particular interest is the interaction of additives with the LAS paste and the mechanism by which structuring agents produce structured LAS paste. This is useful to industry, as it would help identify alternative, potentially cheaper structuring agents that could be used with LAS paste. This study would also aid in the formulation and process developments of future compact detergent powders by providing a basis for examining paste-structuring in different surfactant paste systems and the possible structuring agents that could be used.

1.5.2 Aims

The objective of this work is to contribute to the understanding of the paste-structuring behaviour of high-active LAS. This will be achieved by studying the effect of various additives on the microstructure of the resultant paste with shear and establishing a relationship between this and its resultant material properties. While the results from this work will be interesting from an industrial perspective, they will also be of scientific interest.

The aims of this work are as follows:

(a) to characterise the microstructure and processing behaviour of LAS paste when sheared with a variety of added salts;

(b) to compare the microstructure and processing behaviour of LAS paste structured with sodium disilicate (currently used in industry), with LAS paste structured in the absence of structuring agents;

(c) to examine the additional effect of process temperature on the microstructure and processing behaviour of LAS paste when sheared with added salts;
(d) to probe the relationship between the microstructure, the processing behaviour and material properties of LAS paste;

1.5.3 Outline

An outline of the thesis structure is presented in this section.

In Chapter 1, an introduction to this thesis was given from an industrial perspective. The industrial importance of LAS, the surfactant-based material studied throughout this work, was emphasised. Following this, the trend to compact detergent powders and shift to manufacturing processes such as agglomeration was discussed. A description of the industrial paste-structuring process using high-active LAS was then given. From this background information the purpose and aims of this research were outlined.

A review of the literature is presented in Chapter 2. It is divided into three main sections. Firstly, the LAS system is defined and the typical composition established. Secondly, the equilibrium phase structures common to surfactant-based systems are outlined with emphasis on the structure of quiescent high-active LAS paste. Following this, experimental studies on the effect of shear on the microstructure and rheology of various well-defined systems as well as high-active LAS are presented from the literature. Emphasis is given to the occurrence of shear-induced Multi-Lamellar Vesicles (MLVs), as these are of particular interest to this work.

In Chapter 3, the materials, equipment and experimental techniques used throughout this work are described. The various salts sheared with high-active LAS are listed, the experimental protocol is outlined and a description of the Cambridge Multi-Pass Rheometer (MPR) with X-ray facility is included. As will be discussed, the MPR has been used as a shearing device as well as a scientific instrument for the in-situ monitoring of the rheological behaviour and microstructure present in the sheared samples. The cryo-SEM technique used for observing the microstructure of the sheared pastes will also be described.

In Chapter 4, the effect of an industrial structuring agent, sodium disilicate, on the rheological behaviour and microstructure of high-active LAS is investigated at various temperatures. Results are compared to those obtained without sodium
disilicate, when high-active LAS is sheared alone. From the results, it is shown that high-active LAS processed at 60 °C requires the addition of sodium disilicate in order for ‘structured’ pastes to form where the ‘structured’ pastes consist of MLV-rich microstructures.

Chapter 5 compares the effect of various MLV-inducing salts when shearing high-active LAS at 60 °C. The results show that pastes with tightly-packed MLV microstructures can appear firm or, surprisingly, soft depending on the size and uniformity of the MLVs. In this chapter, an alternative industrial structuring agent, sodium chloride, is investigated.

In Chapter 6, the MLV microstructures are examined in more detail. The effect of the duration of shear is studied as well as the stability of the MLVs. From the results, the MLVs are shown to become more spherical and smaller with shear. The MLVs are also shown to be metastable in the absence of shear.

Chapter 7 discusses salts inducing non-MLV microstructures with shear. The effect of shearing with salts that have no effect on the rheological behaviour and microstructure of high-active LAS will be examined. Following this, mixtures of a salt that does not induce MLVs and an MLV-inducing salt will be studied. Finally salts causing shear-induced phase separation to occur in high-active LAS will be investigated. The biphasic microstructural nature of pastes processed with these salts will be examined and large worm-like structures, not previously reported in the literature, will be identified.
### Table 1.1. Major ingredients and their function in laundry detergent powders (taken from McKeown, 2001)

<table>
<thead>
<tr>
<th>Ingredient Type</th>
<th>Examples of Ingredient</th>
<th>Main Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic Surfactants</td>
<td>Linear alkylbenzene sulfonates, Tallow alcohol sulfates</td>
<td>Removal of fatty stains</td>
</tr>
<tr>
<td>Nonionic Surfactants</td>
<td>Tallow alcohol ethoxylates</td>
<td>Foam inhibition and control</td>
</tr>
<tr>
<td>Builders</td>
<td>Sodium carbonate, Sodium triphosphate, Zeolites</td>
<td>Removal of calcium and magnesium ions from solution; provide a physical framework for the powder</td>
</tr>
<tr>
<td>Fillers</td>
<td>Sodium sulfate, Water</td>
<td>Diluent; processing aid</td>
</tr>
<tr>
<td>Bleaches</td>
<td>Sodium perborate, Sodium percarbonate</td>
<td>Removal of organic colours</td>
</tr>
<tr>
<td>Specific Additives</td>
<td>Sodium silicate, Sodium carboxymethylcellulose, Alkylolamides, Protease enzymes, Sodium soaps, Tetra-acetyl ethylene diamine, Polycarboxylates, Distyryl biphenyl derivatives, Perfumes</td>
<td>Corrosion inhibition, Anti-redeposition of soils, Foam boosting and stabilisation, Removal of proteinaceous stains, Foam inhibition, Bleach activation, Co-builders: enhance zeolites, Fabric and product whitening, Fragrance</td>
</tr>
</tbody>
</table>

### Table 1.2. Formulation (wt. %) of regular powders compared with compact powders, based on typical products from Europe and Japan to demonstrate the large variance in formulations geographically (taken from McKeown, 2001).

<table>
<thead>
<tr>
<th>Ingredient Type</th>
<th>Regular Powders</th>
<th>Compact Powders</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Europe</td>
<td>Japan</td>
</tr>
<tr>
<td>Anionic Surfactants</td>
<td>8 - 12</td>
<td>20 - 22</td>
</tr>
<tr>
<td>Nonionic Surfactants</td>
<td>3 - 5</td>
<td>0 - 3</td>
</tr>
<tr>
<td>Builders and Co-Builders</td>
<td>35 - 40</td>
<td>30 - 35</td>
</tr>
<tr>
<td>Fillers</td>
<td>15 - 25</td>
<td>30 - 35</td>
</tr>
<tr>
<td>Bleaches and Activators</td>
<td>15 - 25</td>
<td>0 - 10</td>
</tr>
<tr>
<td>Specific Additives</td>
<td>2 - 7</td>
<td>0 - 5</td>
</tr>
</tbody>
</table>
Figure 1.1. Generalised flow diagram of the manufacture of LAS-based heavy-duty compact laundry detergent powders (from McKeown, 2001).
Chapter 2

LITERATURE REVIEW

As outlined in the previous chapter, the manipulation of the material properties of high-active LAS paste is essential for the production of compact detergent powders. The macroscopic material properties and rheology (flow and deformation behaviour) are determined by the underlying microstructure of the material. The microstructure is controlled by the composition of the system, temperature and pressure, and can be affected by the application of shear during processing. Thus it is necessary to study the relationship between microstructure and macroscopic properties and the role of structuring agents in controlling paste properties to understand the industrial paste-structuring process.

The literature reviewed in this chapter is in three main sections. The first part gives the typical composition of LAS, thus defining the surfactant-based system that is the focus of this thesis. The second section outlines equilibrium phase structures that are pertinent to surfactant systems, beginning with the principle molecular structure and then increasing the complexity to consider phase and colloidal structures. Special attention is given to the lamellar phase structure and the structure of quiescent high-active LAS paste. The third part of the literature survey presents the results from experimental studies investigating the effect of shear on the structure and rheology of the lamellar phases of various well-defined systems and also on high-active LAS paste. Some of the current theories for shear-induced phenomena are briefly mentioned. Finally, the contribution of this dissertation to the literature will be presented.


2.1 Composition of High-Active LAS

Specifying the composition of high-active LAS is not straightforward – due to many factors, LAS is not always consistent in composition. There are various manufacturing routes for producing LAS, often using impure feedstocks that are variable, resulting in a variety of unwanted products from chemical side-reactions. The available literature often describes LAS vaguely in terms of parameters that are of interest in detergency: average molecular weight, distribution of the carbon chain length, 2-phenyl isomer content and percentage of unsulfonated material. Detergent manufacturers usually specify the main characteristics that are required for commercially used LAS, and this can differ between particular products and companies.

In the manufacturing route commonly used for LAS, the choice of reagents for each stage determine final composition. Briefly, the route is as follows: linear alkylbenzene (LAB) is formed from benzene, LAB is then converted to LAB sulfonic acid (HLAS) via a sulfonation stage and finally HLAS is neutralised to form a mixture of linear alkylbenzene sulfonate salts (LAS) also known as ‘active matter’. These LAS salt molecules make up the bulk of the organic matter in the LAS paste, the rest consisting of organic molecules and inorganic salts formed from side reactions, unreacted material and water. The molecular structures of typical organic compounds found in LAS are shown in Figure 2.1. A description of the composition of LAS is given in the following sections; further details are given by McKeown (2001).

2.1.1 Active Matter

In LAS, the active matter consists of a mixture of alkylbenzene sulfonate surfactant molecules. These molecules are usually in the form of the sodium salt (Matheson, 1996) and are a complex mixture of isomers, varying in carbon (alkyl) chain length, position of the phenyl and sulfonate groups and degree of branching. These factors will be considered separately.
2.1.1.1  **Carbon Chain Length Distribution**

The alkyl chain length distribution of LAS isomers is an important factor in determining performance and formulation characteristics of LAS (Matheson, 1996). The distribution of alkyl chain lengths is already present in the molecules of LAB, from which LAS is made. Laundry detergent powders typically use LAS with a distribution of alkyl chain lengths of C_{11} to C_{15} (Davidsohn and Milwidsky, 1987). The typical chain length distributions of LAB products manufactured by different routes are given in Table 2.1.

2.1.1.2  **Phenyl Group Positional Isomers**

Phenyl isomers are molecules that differ in the position at which the benzene ring (or phenyl group) is attached to a carbon atom along the alkyl chain of the LAS or LAB molecule. The distribution of phenyl isomers can affect the detergency as well as the stickiness of LAS (Davidsohn and Milwidsky, 1987). Depending on the alkylation reaction used to produce LAB from benzene, there are a number of phenyl isomers that can result. Typically the benzene group can be attached to any of the carbon atoms in the alkyl chain, except the terminal ones. Some processes have modifications to increase 2-phenyl isomer as it has preferred properties for certain applications (Modler *et al.*, 1999). Table 2.1 includes the typical 2-phenyl isomer content for LAB products from different feedstocks produced by different routes, while Table 2.2 gives the typical distributions of phenyl isomers for dodecylbenzene (a molecule of LAB) that are produced when different catalysts are used in the alkylation process.

2.1.1.3  **Sulfonate Group Positional Isomers**

In the sulfonation of LAB to form HLAS, the use of a falling film reactor with sulfur trioxide (SO_{3}) is the predominant method (Capeci and Welch, 1998), although sulfonation with concentrated sulfuric acid or oleum is also possible. The sulfonation with SO_{3} results in the predominantly *para*-substituted isomer of HLAS (Davidsohn and Milwidsky, 1987).
2.1.1.4 Branched Isomers

LAB is produced from either linear paraffins or olefins, derived from petroleum (Modler et al., 1999; Davidsohn and Milwidsky, 1987). The branched isomers are undesirable due to the non-biodegradability of the sulfonated product (ABS) thus their presence in LAS is usually minimised. Typically, branched isomers represent 1 to 3% of the LAB product, though this can be as high as 8% (McKeown, 2001).

2.1.2 Water

Aqueous sodium hydroxide (NaOH) is often used to neutralise HLAS to LAS. Water is a by-product of the neutralisation stage, and can also be added during this process to give the desired concentration of active matter in the resultant LAS (Davidsohn and Milwidsky, 1987). The concentration of water in LAS has a significant effect on the physical properties of the system. In Table 2.3, physical properties are given for LAS pastes with varying surfactant concentrations. The viscosity of LAS at a given shear rate increases with increasing active matter content; the viscosity decreases with increasing temperature. For high-active LAS paste typically used in the paste-structuring process (ca. 20% water), the viscosity is high (2.8 Pa s at a shear rate of 30 s\(^{-1}\)) even at an elevated temperature of 70 °C.

2.1.3 Impurities

In LAS, the presence of impurities is inevitable, arising from unreacted reagents and side reactions in the manufacture of LAS.

2.1.3.1 Compounds from Side Reactions

The particular by-products that are formed depend on the impurities that are present in the feedstock used for producing LAS. Figure 2.1 shows the molecular structures of the more common organic by-products in LAS. These compounds are formed at each stage of the LAS manufacturing process. For example, at the beginning of the manufacturing process, during the alkylation of benzene to LAB, compounds such as dialkylbenzenes, diphenylalkanes, dialkyltetralins and
dialkyldianes can be formed (Davidsohn and Milwidsky, 1987). When LAB is sulfonated with SO₃ sulfonic anhydrides, sulfones and disulfonic acids are also produced, forming less than 2% of the product (Woollatt, 1985). In addition to the organic by-products, inorganic salts appear in LAS. For example, during the neutralisation of HLAS to LAS, sodium sulfate is often produced when unreacted sulfuric acid from the sulfonation step reacts with sodium hydroxide (Woollatt, 1985).

2.1.3.2 Unreacted Reagents

In the manufacture of LAS there are a number of processing steps, each using particular reagents and catalysts; traces of these may remain in the final LAS product. Un sulfonated organic compounds such as LAB are often still present after processing and are known collectively as ‘free oil’ (Davidsohn and Milwidsky, 1987).

2.1.4 Summary

LAS is primarily a mixture of alkybenzene sulfonate molecules associated with sodium ions and water, with impurities also present. The active matter is comprised of alkybenzene sulfonate isomers, with linear alkyl chains between 11 and 15 carbon atoms in length and the phenyl group attached to any carbon along the alkyl chain, except for the terminal one. High-active LAS used in the paste-structur ing process consists of ca. 80% active matter in water. However, the impurities that are present may vary between batches depending on the feedstocks and manufacturing routes used. It is evident that with such a complex surfactant system, establishing the microstructure of LAS in the form of a complete phase diagram is difficult as this is determined by its composition. This may also account for the limited amount of published work involving high-active LAS, though there are many of studies carried out on better-defined surfactant systems. In the next section, important structural concepts for surfactant systems at equilibrium will be discussed. The structure of high-active LAS will also be presented at conditions of industrial relevance.
2.2 Self-Assembled Structures in Surfactant Systems

In Section 2.1, the molecular composition of LAS was examined. This section is concerned with the microstructure of high-active LAS at equilibrium: an understanding of the equilibrium phase structure will serve as a foundation for studies of shear-induced phenomena. A hierarchy of structural complexity for self-assembled surfactant systems will be discussed (Table 2.4), beginning with a molecular basis. General structural concepts will be covered before experimental results for the microstructure of high-active LAS at equilibrium are reported from the literature.

2.2.1 General Concepts

High-active LAS can be thought of simply as a system of ca. 80% linear alkybenzene sulfonate molecules in water.

2.2.1.1 Molecular Structure

In high-active LAS, the linear alkybenzene sulfonate isomers that are present in the active matter of the system are surfactant molecules. Surfactants (surface active agents) are molecules that accumulate at interfaces thus modifying the surface properties of materials. They possess an amphiphilic molecular structure with two distinct parts: one that has affinity for the solvent and the other that does not (Clint, 1992). In the LAS system, surfactant molecules are in an aqueous solvent; the anionic (negatively-charged) sulfonate head group is hydrophilic and the linear hydrocarbon tail group is hydrophobic. A schematic diagram of the 2-phenyl-dodecylbenzene sulfonate molecule predominant in LAS systems is shown in Figure 2.2 (a) & (b). The amphiphilic nature of the molecules results in their self-assembly into particular structural aggregates (phase structures) that are present at equilibrium. Although the nature of the molecule influences phase structure, macroscopic rheological properties such as viscosity are more directly influenced by the phase and colloidal levels of microstructure in the system (Laughlin, 1994).
2.2.1.2 Phase Structure

Laughlin (1994) regards phase structure as ‘the manner in which molecules are arranged in space within a phase’. Thus the spatial organisation and orientation of molecules relative to each other are important features of the microstructural arrangements existing in each phase. An equilibrium phase diagram of a surfactant-based system is a means of illustrating the range of temperatures, pressures and compositions within which certain phases occur.

Figure 2.3 illustrates the main features of a typical phase diagram for a surfactant-based system. The Krafft solubility boundary is an important feature, marking the conditions at which the solid surfactant crystal becomes insoluble in an aqueous solution of surfactant monomers. At the Krafft temperature ($T_K$), a sharp increase in solubility is observed. The physical state of the surfactant molecules dissolved in water is dependent on the temperature and also surfactant concentration: below the critical micelle concentration (cmc) surfactants exist as separate molecules, above this concentration the molecules aggregate, forming spherical micelles (Clint, 1992). At high surfactant concentrations, liquid crystals are often formed; they can be regarded as arising from the interactions between micelles at high surfactant concentrations (Tiddy, 1980). These liquid crystals are lyotropic and differ from thermotropic liquid crystals, as they require a solvent to form (Collings and Hird, 1997). The major factors that are important in the formation of particular lyotropic phase structures are electrostatic interactions, surfactant head group hydration, steric repulsions and alkyl chain conformations (Tiddy, 1980).

Liquid crystalline materials possess a degree of molecular ordering which lies between that found in liquids, and in crystalline solids. The molecules in a liquid diffuse about in random directions whereas in a crystal the molecules occupy specific sites in a three-dimensional lattice and are confined to particular positions and orientations. In liquid crystalline phases however, long-range molecular diffusion can occur while some degree of orientational and long-range positional order is retained (Collings and Hird, 1997). These characteristics result in mechanical properties that are intermediate between those of a liquid and those of a crystal (de Gennes and Prost, 1993).
There are three classes of lyotropic liquid crystalline phase structures that are widely recognised: the lamellar, hexagonal and cubic phases (Collings and Hird, 1997). McKeown (2001) has reported that for high-active (ca. 80 % surfactant) LAS paste (at 25 °C and 60 °C) a predominantly lamellar phase exists. The work in this dissertation is thus concerned with the behaviour of the lamellar phase present in high-active LAS. It is therefore appropriate to examine the lamellar phase structure more closely in this section.

◊ Lamellar Liquid Crystal Phase Structure

The lamellar phase is a layered structure, shown schematically in Figure 2.2 (c), where there is one-dimensional long-range order in the direction of the bilayer normal, \( \mathbf{n} \) (Laughlin, 1994). In a LAS-based system, the amphiphilic surfactant molecules form a stacked series of extended planar bilayers, where each bilayer is separated by a water layer.

An individual bilayer structure consists of two surfactant monolayers. Each monolayer consists of surfactant molecules that are arranged adjacent to one another with the long axis of each molecule pointing in the direction of the bilayer normal and the surfactant head groups arranged ‘head-to-head’ to form a planar structure. In a bilayer structure, the two planar monolayers are arranged diametrically so that the hydrophilic surfactant head groups face outwards, while the hydrophobic alkyl tails of the surfactant molecules lie at the centre of the bilayer, shielded from the water layer.

The distance between adjacent bilayers is well-defined and can be characterised by an inter-lamellar distance or fundamental repeat spacing (Figure 2.2 (c)) although undulations are often present in the layers. For a given sample, the thickness of each water layer is the same (typically from 8-100 Å) and the surfactant layer thickness is generally 10-30 % less than the length of two surfactant chains in the \( \text{trans} \) configuration (Tiddy, 1980). The aggregation of surfactant molecules in the lamellar phase and stabilisation of the resultant structures are the result of various forces occurring within and between the aggregate structures as well as the molecular packing geometry (Israelachvili, 1985). These factors will be considered in the following section.
Factors Driving Self-Assembly of Surfactant Molecules

For an aqueous surfactant system such as high-active LAS, different phase structures of well-defined surfactant aggregates readily form depending on the solution conditions. Within the aggregates, van der Waals, hydrophobic, hydrogen-bonding and screened electrostatic interactions result in forces that hold the molecules together. Thus, if the solution conditions, such as electrolyte concentration and pH, change the forces within the aggregate (as well as between aggregates) will be modified resulting in a change of the size and shape of the molecular aggregates (Israelachvili, 1985).

The major forces driving self-assembly in aqueous amphiphilic surfactant solutions arise from the hydrophobic interaction at the hydrocarbon-water interface and the preference of the hydrophilic head groups to be associated with water. These interfacial forces determine effective area, $a_o$, of the surfactant head group per molecule that is exposed to the aqueous phase. The attractive hydrophobic interaction is mainly due to the interfacial tension forces acting at the hydrocarbon-water interface, this force causes the molecules to associate and reduces the value of $a_o$. Repulsive forces that increase $a_o$ are a combination of electrostatic (double-layer) repulsion between charged head groups, hydration repulsion and steric head group and chain interactions. The optimum area per head group is established when attractive and repulsive forces are balanced (Israelachvili, 1985).

The formation of particular aggregate structures is dependent on the geometric packing properties of the molecules. When the geometric or packing properties of the system are considered, the optimum $a_o$, the volume ($v$) and effective length ($l_c$) of the hydrocarbon chains are important factors. A packing parameter given by $v/a_o l_c$ can be defined for various phase structures. In the lamellar bilayer phase, surfactant molecules have a critical packing parameter of ~1 (Israelachvili, 1985).

Intermolecular Forces Between Lamellar Bilayers

In bilayer structures present in the lamellar phase, the main intermolecular forces existing between the bilayers include the attractive van der Waals force, repulsive electrostatic double-layer force, and hydration forces (Israelachvili, 1985).
In aqueous solutions, the van der Waals force between bilayers is generally insignificant in comparison to the electrostatic double-layer repulsion force. When the distance between two bilayers is small (i.e. below ca. 30 Å), repulsive hydration forces may dominate, depending on the hydrophilicity of the surface groups.

2.2.1.3 Colloidal Structure

The phase structure is the highest level of structure that is fully defined by thermodynamics and is a fundamental property of state. While the phase structure is an equilibrium state, the colloidal structure is more complex; more than the composition of the system and system variables are required to define this level of structure. Structure at the colloidal level can be described as ‘the manner in which coexisting phases are arranged in space’ (Laughlin, 1994).

In a system consisting of a single phase, the colloidal structure may consist of an assembly of domains; these are the result of structural defects, which interrupt the continuity of the ordered regions within a particular phase creating boundaries between the domains. Impurities tend to concentrate at the domain boundaries. Within each domain, ‘single-crystal-like order’ exists (Laughlin, 1994); a domain of the lamellar phase can consist of planar bilayers (or lamellae) where the bilayer normal, n, points in a particular direction. A material with a large number of defects can exist in a multi-orientation state, where the domains are arranged with their bilayer normal pointing in different directions (Figure 2.2 (d)); this type of material resembles a crystalline powder sample where the orientation of crystals occurs in all directions. The domain structure persists for long durations within liquid crystal phases that are both highly structured and very viscous. However, defects present in phases of low viscosity rapidly disappear (Laughlin, 1994).

The lamellar phase can also be arranged into other colloidal structures; these include multi-lamellar vesicles (MLVs) and uni-lamellar vesicles (ULVs). MLVs are comprised of many bilayers arranged into an ‘onion-like’ spherical structure while ULVs are closed spherical structures consisting of only one bilayer (Figure 2.4). Micelles are also spherical structures. Instead of a bilayer, a
monolayer of surfactant molecules is present; the hydrophobic chains form a central core with the hydrophilic head groups forming a micellar corona.

In the literature, vesicular structures (particularly ULVs) have been reported to occur ‘spontaneously’ and to persist for long periods of time (for some recent studies refer to Lin and Fu, 1996; Grillo et al., 2003). This has led to considerable debate as to whether these structures constitute an equilibrium state, such as that formed by micelles. In a review published by Laughlin (1996) which involved analysis of the physical science of spontaneous vesicle-forming systems, it was concluded that these structures were unlikely to constitute a true equilibrium state.

There has recently been considerable interest in the use of mechanical shear to form vesicles (particularly MLVs) from lyotropic lamellar phases. Many studies in the literature have been concerned with these out-of-equilibrium transitions; for reviews on recent work, refer to Mortensen (2001) and Richtering (2001). In this thesis, shear-induced MLVs from high-active LAS feature significantly; hence further consideration of the literature regarding shear-induced MLVs will be presented in Section 2.3.

2.2.2 Structure of Quiescent High-Active LAS

After discussing the general concepts relating to structures found in surfactant-based systems in Section 2.2.1, the focus will now be on the microstructure of quiescent high-active LAS used industrially for paste-structuring. Results from a study of high-active LAS by McKeown (2001) will be presented, in which a phenomenological approach was taken to ascertain the likely structure of high-active LAS present at industrially useful temperatures.

In its quiescent (unprocessed) state, commercial high-active LAS at 25 °C is a defect-rich, colloidally-structured lamellar phase, characterised by inter-lamellar distances in the order of 30 Å. Planar lamellae are dominant, with MLVs and microscopic entrapped air bubbles scattered throughout the material. These structural characteristics have been observed to be invariant in similar batches of high-active LAS over time.
At 60 °C, the temperature for industrial paste-structuring, quiescent high-active LAS paste continues to possess a predominantly lamellar microstructure with inter-lamellar distances of ca. 30 Å. The phase structure is similar to that present at 25 °C. However, there is a significant change in the fundamental rheological parameters of LAS with temperature, indicating a difference in the quiescent structural state. It has been speculated that in comparison to LAS paste at 25 °C, high-active LAS at 60 °C possesses a lower density of defects (a change in the colloidal structure) and also a higher degree of mobility and disorder in the alkyl chains in the surfactant bilayer.

In Section 2.2.1.3, the formation of MLVs from lamellar bilayers with the application of shear was mentioned. Such a transformation in structure to MLVs has been reported in high-active LAS (McKeown et al., 2003) and related to the change in material properties observed under certain conditions during the conveyance and transport of high-active LAS in factory pipes. This will be further discussed in Section 2.3.1.3.

2.2.3 Summary

In an aqueous anionic surfactant system such as high-active LAS, the molecules are amphiphilic and capable of aggregating into various equilibrium phase structures. Liquid crystalline phases often appear in surfactant-based systems; these phase structures are characterised by a degree of structural order that is intermediate between that of a liquid and a crystalline solid. The lamellar liquid crystalline phase, in its ideal state, consists of surfactant molecules organised into stacked arrangements of planar bilayers. At the more complex colloidal level, the lamellar phase may be organised into domain structures consisting of planar bilayers, or vesicular structures.

High-active LAS is known to possess a lamellar phase structure (with inter-lamellar distances in the order of 30 Å) at 25 °C and also at 60 °C, the temperature used for industrial paste-structuring. At the elevated temperature, high-active LAS is thought to possess a lower density of defects (a change in the colloidal structure) and also a higher degree of mobility and disorder in the alkyl chains in the surfactant bilayer.
Chapter 2: Literature Review

Vesicular structures can be induced from planar lamellar bilayers with the application of shear. The transformation in structure to MLVs has been reported in high-active LAS and has been related to a change in the material properties. In Section 2.3 studies from the literature will be presented relating to the effect of shear on the lamellar phase occurring in various systems with special consideration given to high-active LAS.

2.3 Effect of Shear on the Lamellar Phase

Quiescent high-active LAS exists in the lamellar bilayer phase at temperatures of industrial relevance. The changes to the structure and rheology of lamellar phases under shear have formed the basis of many recent studies found in the literature, which in turn will form the basis of this section. Experimental evidence from various studies will be considered, beginning with the early work on orientation diagrams where the systematic investigation of shear rate on sample microstructure was introduced and important structural transformations identified. Following this, the focus will be on shear-induced orientation, structural transformation to MLVs and the effect of shear on high-active LAS paste itself. Finally, theoretical considerations will be briefly discussed.

2.3.1 Experimental Studies

When shear is applied to the lamellar phase, complex flow and microstructural behaviour is often exhibited. Recently, many of the studies examining these shear-induced transformations have made use of new experimental methods where microstructural characterisation techniques (e.g. X-ray and neutron scattering, nuclear magnetic resonance and small-angle light scattering) have allowed in-situ measurements to be taken as a sample is sheared and rheological data obtained simultaneously. In this section, experimental studies of shear on the lamellar phase will be reported from the literature. Recent reviews on this area of research are given by Butler (1999), Mortensen (2001) and Richtering (2001).
2.3.1.1 Orientation Diagrams – a Starting Point

The pioneering work by Roux and co-workers (Diat et al., 1993 and Roux et al., 1993) investigated the ‘out-of-equilibrium’ steady-state structures formed from a dilute lamellar phase with shear in a couette cell. Depending on the applied shear rate and dilution of the bilayers, different structural orientations were observed. These results were used to form an ‘orientation diagram’ (or dynamic phase diagram), representing the orientation of the structures as a function of shear rate and dilution; diluting the system allowed the repeat distance of the lamellar bilayers to be varied between 40 and 400 Å. In the surfactant-based quaternary system that was studied, three different states of structural orientation were observed with defined dynamic transitional boundaries between the regions. The structural states and associated rheological behaviour are described below.

◊ **State I.** The planar bilayers in this state were aligned so that the direction of the bilayer normal, \( n \), was predominantly parallel to the shear gradient in the couette cell, with many defects moving with the flow in the two directions perpendicular to \( n \). The material in this state behaved as a Newtonian fluid and was very viscous. When the sample was no longer sheared, the State I-type microstructure persisted for only a few hours. With increasing shear rate, an out-of-equilibrium transition occurred, with a shift in orientation corresponding to State II.

◊ **State II.** Here the microstructure of the sample was comprised of an isotropic state of densely-packed multi-lamellar vesicles (MLVs). These structures consist of bilayers that are wrapped around a spherical core in successive equally-spaced layers to form an onion-like structure (Figure 2.4 (b)). The size of the MLVs (typically 1–10 µm diameter) was found to depend on the shear rate; higher shear rates resulting in smaller MLVs. At high shear rates MLVs that were slightly elongated in the direction of the flow were thought to be present. Shear-thinning behaviour was observed for this state: the apparent viscosity decreasing with the MLV size. The MLVs appeared extremely stable without shear and no noticeable change in microstructure occurred even after a few days. At high shear rates, a transition region containing structures characteristic of both State II and State III was found; as the shear rate was increased, the
defects became highly anisotropic and a shift in orientation to State III occurred.

◊ **State III.** The microstructure in this state was similar to State I as planar bilayers appeared once again, with $n$ parallel to the shear gradient. However, no defects were present in the direction of the flow. The relaxation time for the shear-induced structure was less than a few hours and Newtonian behaviour was observed. The viscosity was much lower than State I.

In this study, the regions and boundaries where the structural states occurred were reproducible. It was also found that these results were not affected by the initial state of the system (i.e. random or partial orientation; fresh or ‘used’ sample), though this did affect the time taken to reach steady-state.

Shear-induced transformations similar to those studied by Roux and co-workers have been found to occur in other systems. In the ternary surfactant system studied by Läuger *et al.* (1996), the three different structural states observed by Roux and co-workers were also present as a function of shear rate, however the rheological behaviour differed slightly. At low shear rates the system exhibited shear-thinning behaviour; with the transition to the MLV state an increase in viscosity was observed although shear-thinning behaviour followed. In the simpler nonionic surfactant system studied by Le *et al.* (2000, 2001a,b), a biphasic planar lamellar/MLV state was observed in addition to a continuous “sponge-phase” and temperature was seen to have a critical effect. Studies by Schmidt *et al.* (1998, 1999) and Zipfel *et al.* (1999) investigated the effect of shear on polymeric surfactant systems. In these systems shear-thickening was found to occur at low polymer concentrations (due to MLV formation from planar bilayers), however at high polymer concentrations, the viscosity decreased with shear, due to the orientation of planar lamellae.

It is evident that the occurrence of orientated planar bilayers and MLVs in sheared samples is widespread. In Sections 2.3.1.2 and 2.3.1.3, aspects of these shear-induced microstructures will be discussed further and in Section 2.3.1.4 the focus will be on the shear-induced microstructures formed by high-active LAS.
Chapter 2: Literature Review

2.3.1.2 Orientation of Planar Lamellae

The shear-induced orientation of planar lamellar phases has been reported in many lyotropic systems. In addition to lyotropic lamellar systems, shear-induced reorientation transitions have also been observed in lamellar block-copolymers (Hamley, 2001), and thermotropic ‘smectic-A’ (layered) liquid crystals (Safinya, et al., 1993). The alignment of the planar layers is usually described in terms of the orientation of the layer normal, \( n \), following the notation adopted by Safinya et al. (1993) for experiments conducted in a couette cell geometry. Three perpendicular orientations are defined depending on whether \( n \) points along the neutral (or vorticity) direction, flow direction or shear gradient direction (Figure 2.5) and can be termed as \( a \) (‘perpendicular’), \( b \) (‘transpose’) or \( c \) (‘parallel’) orientations respectively (Zipfel et al., 1999).

For a range of surfactant-based systems, planar bilayers aligned in orientation \( c \) are generally found at ‘low’ shear rates (Diat et al., 1993; Soubiran et al., 1995; Lukaschek et al., 1996; Läuger et al., 1996; Penfold et al., 1997a,b; Zipfel et al., 1999). At ‘high’ shear rates the \( c \) orientation (Diat et al., 1993; Safinya et al., 1993; Soubiran et al., 1995; Läuger et al., 1996) and \( a \) orientation (Penfold et al., 1997a,b; Zipfel et al., 1999) have been observed. A mixed state with lamellae co-existing in both the \( a \) and \( c \) orientations has also been reported (Penfold et al., 1997a; Zipfel et al., 1999).

2.3.1.3 Formation of Multi-Lamellar Vesicles (MLVs)

Surfactant systems existing in the lamellar phase can be sheared to form MLVs. A major factor in MLV formation is thought to be the defect texture of the lamellar phase (Diat and Roux, 1993; Zipfel et al., 1999). The MLV phase itself can be considered a lamellar phase with a well-defined concentration and distribution of defects in the texture (Zipfel et al., 1999). During the formation of MLVs, rheopectic behaviour has been reported in a number of systems (Bergenholtz and Wagner, 1996; Läuger et al., 1996). Shear-thinning behaviour has also been observed in the vesicle phase region itself (Roux et al., 1993; Läuger et al., 1996).
There are a number of factors that influence the formation and structural characteristics of MLVs in lamellar systems. These include the mechanical deformation applied to the system and also the composition of the system.

◊ Mechanical Deformation

The mechanical deformation applied to a lamellar system can influence the MLV microstructure that may result. As stated in Section 2.3.1.1, the size of the MLVs has been related to the shear rate (Diat et al., 1993) although Bergenholztz and Wagner (1996) regard the shear stress as being the correct factor in determining MLV size. In addition to MLV size, the arrangement of MLVs in the sample is dependent on the shearing conditions; an ‘amorphous’ or glassy arrangement of MLVs can form (Diat et al., 1993) or an ordered arrangement of MLVs in a close-packed hexagonal lattice can appear (Diat et al., 1995).

In the glassy arrangement of MLVs, high shear rates have been shown to deform the MLVs in the direction of the flow (Diat et al., 1993; Läuger et al., 1996; Zipfel et al., 1998). Sierro and Roux (1997) found that for an ordered arrangement of MLVs, an increase in the shear rate resulted in a transition from an ordered MLV phase with small vesicles to an ordered phase of larger vesicles.

It is also possible to have biphasic microstructures where MLVs coexist with planar lamellae; these have been observed for various systems (Le et al., 2001b, Bergenholztz and Wagner, 1996). It has been proposed by Bergenholztz and Wagner (1996) that applying a controlled shear rate to a lamellar system will result in a biphasic state of orientated planar lamellae and MLVs whereas a pure MLV phase is attainable with a stress-controlled rheometer.

◊ Composition

There have been studies in the literature examining the behaviour of lamellar systems with shear when the composition of the system is varied. The relative concentration of the surfactant to the other components in the system determines the lamellar repeat distance within the sample microstructure. In the literature, MLVs have been induced with shear from lamellar systems with bilayer repeat distances typically ranging anywhere from between ca. 30 to ca. 500 Å; high-active LAS has a relatively small lamellar repeat distance of ca. 30 Å. In
addition to surfactant concentration, salinity and charge density have also been the subject of study.

In the investigation by Lukaschek et al. (1996), rheo-NMR techniques were used to study the lamellar phases of concentrated aqueous ethylene oxide surfactants (35, 60 and 80 wt. %). They found that for a thermodynamically-stable lamellar phase of planar layers, the MLVs that form with shear revert back to their original planar state when shear is no longer applied and that the surfactant concentration affected the stability of the vesicles. They also found the shear history of the sample to be important.

Gradzielski et al. (1997, 1999) studied the surfactant system of sodium oleate/octanol/water. The co-surfactant (octanol) was found to induce a stiff gel-like phase of densely-packed uni-lamellar vesicles for a particular ratio of octanol to sodium oleate and above a minimum concentration of sodium oleate. Decreasing the carbon chain length of the co-surfactant was found to result in the thickness of the bilayer decreasing. Above a critical length vesicles did not form.

Bergmeier et al. (1999) investigated the aqueous system TDMAO/TTABr/n-hexanol [TDMAO – tetradecyldimethylamine oxide and TTABr - tetradecyltrimethylammonium bromide] and found that, at low TTABr content, preferentially planar lamellae were formed, while MLVs appeared at higher TTABr content. Shearing the system transformed the planar lamellae to MLVs – an increase of the shear rate caused vesicle shells to be stripped off, and at high shear rates uni-lamellar vesicles were formed. Their interpretation was that the lower the charge density of the system, the greater the resistance to the mechanical stress caused by a shear field; for systems with a greater charge density, the increased tendency to form highly curved interfaces.

The effect of salinity on flow-structure properties in a lamellar system was studied by Léon et al. (2000). A dilute AOT/water/NaCl system [sodium bis(2-ethylhexyl) sulfosuccinate (AOT) surfactant concentration of 7 wt. %] was used for the investigation. They found that at ‘high’ salinity, a low viscosity planar lamellar equilibrium phase existed and that with shear, a sudden transition to a viscoelastic gel occurred. Their observations indicated that the gel consisted of ‘onions’ (MLVs) ‘connected by a network of bilayers’. They postulated that the
high viscosity of this gel phase was due to the different ‘onions’ sharing a certain number of bilayers. It was also found that gelation occurred after a certain delay time and that the delay increased with salinity.

2.3.1.4 Case Study: Effect of Shear on High-Active LAS

There have been a few investigations on the effect of shear on high-active LAS (McKeown, 2001 and McKeown et al., 2003). The main results from these studies will be outlined in this section as these have formed the basis of the present work. The studies carried out by McKeown and coworkers used the MPR in multi-pass mode to examine the effect of shear on high-active LAS (without additives). Using the same shearing geometry, the piston speeds (apparent shear rates) were varied and experiments performed at 4 bar static pressure and either 25 °C or 60 °C.

At 25 °C it was found that for processing at a fixed piston speed, the shear-induced structural changes and accompanying rheology were time-dependent and that at higher piston speeds the time required to reach rheological steady state was reduced. At low apparent wall shear rates (11 s\(^{-1}\), 110 s\(^{-1}\), 1,100 s\(^{-1}\)) the formation of densely-packed MLVs accompanied by rheopectic behaviour was observed, and sheared samples appeared (by visual and manual inspection) to be ‘structured’. At high apparent wall shear rates (5,700 s\(^{-1}\), 11,000 s\(^{-1}\)) the behaviour of high-active LAS was dominated by the orientation of the planar lamellar microstructures parallel to the flow direction; thixotropic behaviour was observed and the sheared samples appeared ‘unstructured’.

During multi-pass shear at 60 °C, samples reached rheological and structural steady state more quickly than at 25 °C for the corresponding piston speeds. The values of apparent viscosity were less than half that at 25 °C and shear-thinning behaviour was observed for apparent wall shear rates between 110 and 11,000 s\(^{-1}\). Shear-induced orientation of planar lamellae was observed during multi-pass shear, but the formation of a shear-induced MLV state was not detected by X-ray scattering at any of the piston speeds studied. Observations (by visual and manual inspection) of sheared samples suggested that they were not ‘structured’.

When the experiments were performed at 60 °C and the static pressure was
increased to 30 bar, the results obtained from multi-pass shear showed similar trends to those at 4 bar.

2.3.2 Theoretical Considerations

The behaviour of lamellar systems in the presence of shear flow to form aligned planar bilayers and MLVs has been discussed in Section 2.3.1. Although there have been a number of experimental studies, the theoretical understanding behind such phenomena is still under development.

◊ Orientation of Planar Lamellae

In lamellar systems where the planar lamellae align with shear, the stability of the $a$ and $c$ orientations has been understood from several points of view, however at present it is not clear which mechanisms operate in a given system (Marlow and Olmsted, 2002). Cates and Milner (1989) predicted that shear would stabilise a layered system near a sponge-lamellar phase transition whereas Ramaswamy (1992) predicted that shear flow would suppress undulations in the $a$ orientation resulting in a collapse of the lamellar phase. Goulian and Milner (1995) studied the instability of thermotropic smectics; they noted that convection of bending fluctuations could induce compression which destabilises the $c$ orientation with respect to the $a$ orientation. Fredrickson (1994) showed that non-linearities in the diblock copolymer free energy would also result in destabilising the $c$ orientation relative to the $a$ orientation; another mechanism discussed is viscous contrast, where lamellae aligned in the $c$ orientation allow the strain field to be concentrated in the less viscous material, causing this orientation to be favoured at higher frequencies or strain rates.

◊ Formation of MLVs

Currently, there is no reliable theoretical framework for understanding the MLV-phase (Marlow and Olmsted, 2002). It is thought that the instability giving rise to MLV formation may be analogous to the Helfrich-Hurault mechanism (de Gennes and Prost, 1993), where an applied dilational strain parallel to the layer normals results in buckling of the layers to retain the equilibrium layer spacing. Oswald and Kleman (1982) proposed that the dilational strain could be
induced from the defects generated as a lamellar or smectic system flows between misaligned plates. Wunenburger et al. (2000) considered the transition from MLVs to aligned planar lamellae at high shear rates, demonstrating that with high enough shear rates, an undulation could persist in the velocity gradient direction while a restabilisation would occur in the velocity direction.

2.3.3 Summary

In this section, a review of studies in the literature examining the effect of shear on various lamellar systems has been presented. From the initial work on orientation diagrams, it was found that for a particular lamellar system, shear-induced transformations were dependent on the applied shear rate and system composition (dilution). Similar behaviour has also been observed in other lamellar systems. From experimental studies, common shear-induced transformations are aligned planar bilayers and MLV microstructures, although biphasic structures can also result. Factors such as the mechanical deformation and composition of the lamellar system have been shown to affect the formation of MLVs from the planar lamellae. Studies on high-active LAS (without additives) have shown that its behaviour is dependent on the applied shear rate and temperature. The formation of MLVs from high-active LAS has been shown to occur at 25 °C and ‘low’ shear rates, with aligned planar lamellae forming at 25 °C and ‘high’ shear rates and also at 60 °C for all the shear rates investigated. Experimental studies have contributed significantly to the understanding of shear-induced phenomena. Satisfactory theoretical models, particularly for MLV formation, are yet to be developed.

2.4 Chapter Summary

In this chapter, a review of the relevant literature has been presented. As LAS exists as a complex system of various molecular isomers and impurities in water, a typical composition of the industrial material was given. Structural characteristics pertinent to a surfactant system were then considered beginning with an amphiphilic surfactant molecule, and then building up to the phase and colloidal levels of structure. Following this, the structure of quiescent
(unsheared) high-active LAS was described: a lamellar phase structure (with inter-lamellar distances in the order of 30 Å) at 25 °C and also at 60 °C, the temperature used for industrial paste-structuring. Studies in the literature on the effect of shear on the lamellar phase were then summarised. From experimental investigations examining a variety of systems including high-active LAS, aligned planar bilayers and MLV microstructures were found to occur depending on the shear rate or shear stress. In addition, temperature and composition were also found to be important factors. At present a complete theoretical model for MLV formation is yet to be developed.

2.5 Contribution of Current Research to the Literature

The literature provides an interesting background for this study of high-active LAS. McKeown (2001) was the first to observe shear-induced transformations occurring in this industrial surfactant system, particularly the formation of MLVs and the effect on the rheology of the system. However, there has been no scientific investigation on the effect of various salts on the shear-induced behaviour of high-active LAS. There are a number of questions that arise when salts are added to the system during shear. For example, it is not known whether the salts will affect the bilayer repeat distance, or if the cations/anions have different effects on the microstructure and rheology of the system. Thus the research in the present study serves not only to understand the industrial paste-structuring process better, but also contributes to the scientific understanding of the factors affecting MLV formation.
Table 2.1. Typical compositions of linear alkylbenzene (LAB) products of comparable average molecular mass, produced by different manufacturing routes. HF and AlCl₃ refer to hydrogen fluoride and aluminium chloride, respectively, used in the alkylation of benzene. Taken from McKeown (2001).

<table>
<thead>
<tr>
<th>Manufacturing Route</th>
<th>Catalyst System</th>
<th>Linear Feedstock</th>
<th>HF Olefins</th>
<th>AlCl₃ Chloroparaffins</th>
<th>AlCl₃ Olefins</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HF Olefins</td>
<td>AlCl₃ Chloroparaffins</td>
<td>AlCl₃ Olefins</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average Molecular Mass (g mol⁻¹)</td>
<td>240</td>
<td>241</td>
<td>240</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear Alkylbenzenes (wt. %)</td>
<td>93</td>
<td>88</td>
<td>98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Phenyl Alkanes (wt. %)</td>
<td>18</td>
<td>29</td>
<td>29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dialkyltetralins (wt. %)</td>
<td>0.5</td>
<td>9</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkyl Chain Distribution (wt. %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₀</td>
<td>14</td>
<td>13</td>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₁</td>
<td>34</td>
<td>30</td>
<td>29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₂</td>
<td>31</td>
<td>30</td>
<td>32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₃</td>
<td>20</td>
<td>25</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₄</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2. Distributions (wt. %) of phenyl group positional isomers of dodecylbenzene from the alkylation of benzene with 1-dodecene in the presence of anhydrous catalysts. Taken from McKeown (2001).

<table>
<thead>
<tr>
<th>Catalyst System</th>
<th>Phenyl Group Position Along the Alkyl Chain</th>
<th>Hydrogen Fluoride</th>
<th>Aluminium Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2-</td>
<td>20</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>3-</td>
<td>17</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>4-</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>5-</td>
<td>23</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>6-</td>
<td>24</td>
<td>15</td>
</tr>
</tbody>
</table>
Table 2.3. Typical physical properties of LAS pastes with various active matter contents. Taken from McKeown (2001).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>White, opaque, very viscous liquid</td>
</tr>
<tr>
<td>Viscosity at 30 s⁻¹ (Pa s)</td>
<td>2.0 at 40 ºC, 40 % active matter</td>
</tr>
<tr>
<td></td>
<td>3.5 at 40 ºC, 55 % active matter</td>
</tr>
<tr>
<td></td>
<td>1.2 at 60 ºC, 40 % active matter</td>
</tr>
<tr>
<td></td>
<td>1.6 at 60 ºC, 55 % active matter</td>
</tr>
<tr>
<td></td>
<td>2.8 at 70 ºC, ca. 80 % active matter</td>
</tr>
<tr>
<td>Heat Conductivity (W m⁻¹ ºC⁻¹)</td>
<td>0.40 at 40 % active matter</td>
</tr>
<tr>
<td></td>
<td>0.38 at 45 % active matter</td>
</tr>
<tr>
<td></td>
<td>0.35 at 50 % active matter</td>
</tr>
<tr>
<td>Specific Heat (kJ kg⁻¹ ºC⁻¹)</td>
<td>3.2 at 40 % active matter</td>
</tr>
<tr>
<td></td>
<td>3.1 at 45 % active matter</td>
</tr>
<tr>
<td></td>
<td>3.0 at 50 % active matter</td>
</tr>
<tr>
<td>Density (kg m⁻³)</td>
<td>ca. 1000, variable with active matter concentration</td>
</tr>
</tbody>
</table>

Table 2.4. Levels of structure in lyotropic liquid crystalline surfactant-based systems. Taken from McKeown (2001).

<table>
<thead>
<tr>
<th>Levels</th>
<th>Structure</th>
<th>Typical Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular</td>
<td>Surfactant molecule</td>
<td>Few nm × 0.1 nm</td>
</tr>
<tr>
<td>Phase</td>
<td>Lamellar</td>
<td>^aFew nm to few 100 nm</td>
</tr>
<tr>
<td>Colloidal</td>
<td>Domain</td>
<td>Few μm</td>
</tr>
</tbody>
</table>

^aInter-lamellar distance
Figure 2.1. Examples of the molecular structures of some of the organic compounds potentially found in LAS. R represents a linear alkyl group of the form -CH$_2$(CH$_2$)$_n$CH$_3$, where n is an integer. Where there is more than one R group in the same molecule, the R groups do not necessarily have the same value of n. Taken from McKeown (2001).
Figure 2.2. Schematic diagrams showing different levels of structure for a binary surfactant-water system: (a) molecular structure of linear 2-phenyl-dodecylbenzene sulfonate and (b) its schematic representation as a surfactant molecule; (c) phase structure of the lyotropic lamellar liquid crystal composed of low molecular weight surfactants in water; (d) colloidal structure of a defect-rich lamellar liquid crystal of a single-phase mixture, showing randomly oriented domains. After McKeown (2001).
Figure 2.3. Schematic phase diagram for a typical surfactant (soap) in water. The phase diagram has been generalised to emphasize the key features and to show that at constant pressure a range of phases can be formed depending on the temperature and surfactant concentration. The boundary positions and presence of particular phases vary according to the system examined; \( L_1 \), \( H_1 \), and \( L_\alpha \) represent the normal micellar phase, the normal hexagonal phase, and the lamellar phase, respectively. The Krafft temperature \( T_k \) marks a sudden jump in the solubility of the surfactant crystal. At temperatures above \( T_k \), molecules can form micelles when the surfactant concentration exceeds the critical micelle concentration. After McKeown (2001).
Figure 2.4. Schematic diagrams of different types of bilayer organisation: (a) planar bilayers; (b) multi-lamellar vesicles (MLVs); (c) uni-lamellar vesicles (ULVs). In this diagram, each line/circle represents a bilayer arrangement of molecules. Taken from McKeown (2001).

Figure 2.5. Schematic diagram showing the directions of the neutral (or vorticity) axis (\(z\)), shear gradient axis (\(\nabla v\)) and flow axis (\(v\)) in a couette cell, and the three bilayer orientations referred to in the text as \(a\), \(b\) and \(c\). After McKeown (2001).
Chapter 3

EXPERIMENTAL SECTION

The purpose of this chapter is to describe the materials, equipment and experimental techniques used for this study. The description of materials will include high-active LAS, the processing of which has formed the basis of this work and various salts used during experiments with LAS. By shearing LAS paste with different additives and observing the resultant microstructure and rheological/material properties, an insight into the mechanisms behind paste-structuring has been gained. The Cambridge Multi-Pass Rheometer (MPR) will also be described; this has been used for shearing the high-active LAS and monitoring its rheological behaviour. In addition, characterisation techniques used for probing the microstructure of processed LAS will be examined; X-ray diffraction and Scanning Electron Microscopy (SEM) have been used extensively for this purpose. Finally, the overall experimental procedure will be outlined, combining the shearing, rheological monitoring, and structural characterisation of high-active LAS with various additives.

3.1 Materials

High-active LAS paste was obtained from Procter & Gamble (Newcastle Technical Centre, England). The chemical composition of typical high-active LAS is given in Table 3.1 for two similar batches; a detailed description of LAS composition can be found in Section 2.1. The results throughout this work are given for a single batch of LAS with an active matter content of 78 wt. %. To prevent any moisture loss, the LAS paste was stored in a sealed container at ca. 18 ºC.

Colloidal sodium disilicate, the structuring agent in industrial paste-structuring, was used for the experiments that will be described in Chapter 4. Colloidal
sodium silicates in solid form are amorphous and known as ‘soluble glass’; they are available commercially as a soluble powder. Colloidal silicates differ from crystalline silicates as they are not distinct stoichiometric chemical substances and may have any ratio of SiO₂/Na₂O from about 1.6 to 3.85: the higher the proportion of Na₂O, the more alkaline the material (Woollatt, 1985). In this work the “Pyramid P70” grade of colloidal sodium silicate powder, with a molar ratio of 2SiO₂:Na₂O, was obtained from INEOS Silicas Ltd (Netherlands). The powder particles were between 65 µm and 250 µm in diameter.

Throughout this work, a variety of different salts were used as additives during the processing of LAS. These are listed, each with their molecular formula and respective suppliers, in Table 3.2. For experimental purposes, the level of sodium disilicate added to 20 g of high-active LAS was 10 wt. %, rather than the typical industrial level of 1 wt. %. Subsequent experiments with NaCl were carried out using 10 wt. % salt, however it was thought that using a mole-basis (0.034 mol Na⁺/20 g high-active LAS) for determining the comparable amount of salt to add would be more appropriate. For the majority of the remaining experiments, the amount of salt added to 20 g of high-active LAS was determined by taking a basis of 0.034 mol of a singly-charged ion (e.g. Na⁺, NH₄⁺, NO₃⁻) in the salt. These amounts (converted back to a weight-basis) can be found in Table 3.2; experiments that were carried out using salt levels different to those listed in Table 3.2 will be discussed in Chapter 5.

### 3.2 The Multi-Pass Rheometer (MPR)

#### 3.2.1 Suitability of the MPR for the Present Work

The Cambridge Multi-Pass Rheometer (MPR) (Mackley et al., 1995) has been used throughout this work as a processing tool for applying a high level of shear to LAS paste and also as a scientific instrument for monitoring its rheological behaviour. The MPR was developed in the University of Cambridge in the Department of Chemical Engineering. Essentially, the MPR (Figure 3.1) is a double-piston capillary rheometer in which the sample is fully enclosed and pressurised. The machine allows for high apparent wall shear rates to be investigated (typically in the order of 10⁵ s⁻¹) and enables the control and
Chapter 3: Experimental Section

measurement of pressure, temperature and flow. In addition, an X-ray unit can be attached to the MPR (version III) allowing \textit{in-situ} X-ray measurements to be obtained (Figure 3.2); this will be further described in Section 3.3.1.

The MPR is well suited for investigating the effect of continuous shear on high-active LAS (McKeown, 2001). An advantage over conventional capillary rheometers (where the sample is passed once through the capillary system) is its capability to reverse the direction of sample flow allowing material to be passed through the system many times. The enclosed sample geometry also prevents centrifugal expulsion of sample material; this is a common occurrence at high shear rates in conventional rotational rheometers (McKeown, 2001).

3.2.2 Description of the MPR

The MPR is a novel processing and analytical tool consisting of three main sections: the upper barrel, lower barrel and central test section (Figure 3.1). Table 3.3 summarises the scope of MPR processing parameters as well as the various test piece geometries that can be used in the test section. In the following paragraphs, a description of the design and operation of the MPR will be presented.

3.2.2.1 MPR Design

Of the three sections in the MPR, the central test section is where the sample material undergoes significant shear deformation. The level of shear varies with factors such as the volumetric flow rate of sample through the test section and the geometry of the test piece. In the present work, a capillary assembly was used in the test section; this consisted of a central capillary insert constructed from carbon-fibre to enable X-ray measurements to be taken (see Section 3.3.1) and stainless-steel capillary inserts on either side. The capillary portion of the test section had an internal diameter of 2 mm and total length of 90 mm (L/D = 45). The capillary assembly was used in the work by McKeown (2001) where it was designed to minimise the extensional deformation of the sample at the entrance of the capillary relative to the shear deformation occurring within the capillary itself. This design was necessary as the Bagley correction, used to correct for entrance
effects in capillary rheometry, could not be applied due to the time-dependent rheological behaviour of LAS (see Appendix B).

In the MPR, the sample material is fully enclosed and pressurised by two pistons that are placed either side of the central test section. The pistons can move separately or together to force the sample through the capillary section, thus shearing the material. A hydraulically-driven servo actuator controls the movement of the pistons and the position of each piston is measured with a linear displacement transducer. Feedback control is achieved via a Proportional, Integral and Derivative (PID) system. Two pressure transducers positioned in the barrel walls on either side of the capillary section measure the pressure difference across the capillary as the sample material is pushed through; the pressure difference is related to the rheological properties of the sample (see Appendix B). The position of the pistons and the pressures on both sides of the capillary can be recorded by the software used with the MPR at time intervals specified by the user and the ‘raw’ data can be exported for analysis in a standard spreadsheet program such as Microsoft Excel. The three sections of the MPR are connected to an oil heating circuit that controls the temperature in the system. During experiments it was not possible to measure the temperature of the sample directly; instead a thermocouple located in the wall of the stainless steel capillary (1.4 mm from the edge of the sample) was used for monitoring the sample temperature near the region examined by X-rays (Figure 3.2 (c)). The temperature measured by the thermocouple gives an estimate of the sample temperature and this was used to set the nominal temperature for experiments.

3.2.2.2 MPR Operation

Control and data acquisition software (programmed in LabVIEW) allow the MPR to be operated in modes where the piston motion is predefined. With the experiments used to process LAS paste, the MPR was used in ‘multi-pass’ mode. A ‘single’ pass or stroke involves pushing sample material through the capillary at a steady volumetric flow rate or piston velocity in one direction. In multi-pass mode this process is repeated many times through a series of steady passes of defined distance in alternating directions. The amplitude is the piston displacement from the midpoint position of the full length of the piston stroke to
either the top or bottom of the piston stroke. The user specifies the time between each piston stroke where the pistons are at rest (idle time). The result is that the sample is forced through the capillary repeatedly. One piston cycle consists of two consecutive single piston passes in opposite directions. Shearing is pseudo-continuous, as the direction of shear is not constant and there is a period of idle time between each piston stroke.

3.2.2.3 Standard MPR Processing Parameters

For the experiments carried out during the course of this work, all the MPR processing parameters were kept constant except for the temperature. The temperature was generally set at 60 ºC (the temperature used in the industrial paste-structuring of high-active LAS) for most of the experiments. In some experiments, additional temperatures of 25, 40, and 75 ºC were also investigated. The capillary assembly for this work has been described earlier; this was used with the following processing parameters in multi-pass mode: piston velocity = 5.1 mm s\(^{-1}\) (corresponding to an apparent wall shear rate of 1,100 s \(^{-1}\)), amplitude = 3 mm and idle time = 0.02 s. Prior to shear, the pistons were used to pressurise the sample to a static pressure of 4 bar.

The MPR parameters were selected from those used in the work conducted by McKeown (2001). It was found that at these conditions, shearing high-active LAS alone at 60 ºC resulted in a microstructure of aligned planar lamellar layers, whereas at 25 ºC, MLVs formed. These parameters provide a basis for studies using the MPR to investigate the effect of various salts on the microstructure and processing/structuring behaviour of high-active LAS at industrially relevant temperatures.

3.2.3 Analytical Methods

In addition to its role as a processing tool, the MPR can be used as a scientific instrument for monitoring the rheological behaviour of samples. The analysis is based on standard techniques used for capillary rheometry. However, in multi-pass mode the multiple piston passes that occur over the course of the experiment
require that additional consideration be given during analysis, especially for samples with time-dependent rheological properties.

3.2.3.1 Aspects of Capillary Rheometry

In capillary rheometry, the pressure difference measured across the capillary during steady flow is related to the apparent wall shear stress (Appendix B). For a Newtonian fluid, assuming no slip at the capillary wall, the wall shear rate can be calculated from the volumetric flowrate. The viscosity is then the (wall shear stress)/(wall shear rate).

It is common in capillary rheometry to use the Bagley correction for correcting for entrance effects occurring at the ends of the capillary. As discussed in Section 3.2.2.1, the capillary assembly was designed to minimise this contribution. For non-Newtonian fluids, Rabinowitsch-Mooney corrections are used to calculate wall shear rates and viscosities. However, due to the time-dependent rheological and structural changes exhibited by high-active LAS, the Rabinowitsch-Mooney corrections are not possible (see Appendix B for further details).

3.2.3.2 Rheological Analysis of MPR Data

With the MPR, as with standard capillary rheometry, rheological information is obtained from the pressure difference across the capillary as the sample is forced through it. From the top transducer pressure ($P_t$) and bottom transducer pressure ($P_b$) measured on either side of the test section, the instantaneous pressure difference across the test section, $\Delta P$ is calculated ($\Delta P = P_b - P_t$).

A typical set of raw data obtained for a single piston cycle operating in multi-pass mode using the processing parameters listed in Section 3.2.2.3 is shown in Figure 3.3 (a) whilst the corresponding graph for calculated values of $\Delta P$ is shown in Figure 3.3(b). In Figure 3.3 (a), as the pistons travel upwards and material is forced through the capillary, $P_b$ increases rapidly to a plateau value that is maintained for the length of the piston pass. During the short period of idle time while the pistons are at rest, there is a rapid decrease in $P_b$; this has been attributed to a combination of viscoelastic and compressibility effects (Ranganathan et al., 1999; McKeown, 2001). On the downward piston pass,
values of $P_t$ increase to a plateau value and a period of idle time follows before the cycle is repeated many times.

In Figure 3.3 (b), values of the pressure difference across the capillary ($\Delta P$) are shown for a single piston cycle. The plateau values of $\Delta P$ during upward and downward piston passes are used to calculate the pseudo-steady state pressure ($\Delta P_p$) by averaging the magnitude of the plateau pressure values for consecutive single piston passes. During multi-pass mode, the piston cycles are repeated many times. For materials exhibiting time-dependent rheological behaviour (such as high-active LAS), $\Delta P_p$ changes after many piston cycles, though during a single piston pass $\Delta P_p$ may appear constant; hence the pseudo-steady state pressure (McKeown, 2001). In view of the time-dependent rheological behaviour previously displayed by high-active LAS, the rheological data obtained from the MPR in this study are displayed as graphs of $\Delta P_p$ plotted against processing time. In these graphs, each $\Delta P_p$ point is an average value and the corresponding shearing time is taken from the beginning of the piston stroke, after the preceding period of idle time.

The aim of this study has not been to determine the specific rheological parameters of processed high-active LAS, but rather to compare the processing behaviour of LAS with different additives, with the aim of understanding the mechanisms underlying the paste-structuring process. Thus, the rheological analysis has been limited to comparing graphs of $\Delta P_p$ against processing time for the standard piston velocity (apparent wall shear rate) used for all experiments. Values of $\Delta P_p$ provide a comparative measure of material properties present in processed LAS paste; it is intuitive that larger values of $\Delta P_p$ correspond to larger values of apparent viscosity (stiffer/firmer pastes). More work would be required to establish the suitability of $\Delta P_p$ as a measure of ‘successful’ paste structuring. For example, in addition to the firmness of structured surfactant paste, the stickiness of the paste is also thought to influence the ability of the paste to form acceptable detergent granules, which is the ultimate aim of the paste structuring process. In the present work, $\Delta P_p$ is used as a measure of the viscosity/firmness of processed LAS paste, but not as an indicator of the stickiness of the paste.
3.3 Structural Characterisation Methods

The MPR is suitable as a processing tool and a means of monitoring the firmness of processed LAS paste. However, in order to obtain data to characterise the microstructure of the processed material, additional techniques are required. Some of the experimental techniques that are often used to investigate the structure of complex fluids, such as high-active LAS, are covered in texts by Larson (1999) and Hamley (2000). The structural characterisation methods used throughout this work are X-ray diffraction and Scanning Electron Microscopy (SEM). The X-ray diffraction measurements were collected in-situ as the paste was sheared in the MPR while SEM analysis of the paste samples occurred after processing.

3.3.1 X-ray Diffraction

X-ray diffraction is a technique that investigates the microstructure of materials and is based on the scattering of X-rays by electrons. Data obtained from X-ray scattering experiments relate to the electron density distribution in the sample and differ for materials of different microstructures. The length of repeating units within the material microstructure as well as the orientation of these units within the sample can be obtained. A brief overview of X-ray scattering theory can be found in Appendix C.

3.3.1.1 X-ray Diffraction Equipment and Experimental Parameters

◊ X-ray Unit Attached to the MPR

The X-ray unit (Bruker AXS, Madison, USA) used for this work was housed in a custom-built cabinet which could be coupled to the MPR (version III); the X-ray unit was operated in transmission mode, enabling in-situ X-ray measurements to be obtained during shearing experiments. In Figure 3.2 (d), the X-ray beam path through the MPR capillary is shown schematically; this is a similar to the setup used by McKeown (2001). The X-ray unit consisted of a Siemens Kristalloflex 760 X-ray generator equipped with a graphite monochromator for CuKα radiation (\(\lambda = 1.5418 \ \text{Å}\)) and a collimator of 0.8 mm diameter. A two-dimensional Siemens HI-STAR detector (active area of 115 mm diameter) was
used to collect the scattered X-rays and a beam-stop with a diameter of 10 mm used to protect the detector from the transmitted beam.

To maximise the detected X-ray beam intensity, the X-ray generator was set at a voltage of 45 kV and current of 45 mA for all experiments and a helium-filled tube placed in the path between the sample and detector to reduce the ‘noise’ due to background scatter from air molecules. The sample-detector distance of approximately 76.3 cm was calibrated using a silver behenate standard \((\text{C}_{22}\text{H}_{43}\text{O}_{2}\text{Ag})\) (Eastman Kodak, Rochester, USA) with its first order peak at 1.51° 2θ and its second order peak at 3.02° 2θ (Blanton et al., 1995).

◊ MPR Capillary for X-ray Measurements

The MPR capillary assembly has been described in Section 3.2.2.1. For X-ray scattering in transmission mode, McKeown (2001) calculated the optimal thickness of a sample of high-active LAS to be 0.7 mm, though a 2 mm diameter capillary was used as it was more practical for aligning the X-ray beam path through the capillary. In this work, a 2 mm internal diameter capillary assembly was also used. However, a carbon-fibre capillary insert was used in preference to the beryllium capillary used by McKeown (2001), as the continued exposure of beryllium with the aqueous paste at elevated temperatures was considered too hazardous.

The carbon-fibre capillary absorbed more of the X-ray beam than the beryllium capillary, however by using the longer exposure time of 300 s (rather than the 120 s used by McKeown (2001)) an adequate statistical count of scattered X-rays from the LAS-based sample was achieved. The carbon-fibre capillary also produced additional scattering close to the central X-ray beam (Figure 3.4 (a)), however as this did not interfere with diffraction exhibited by high-active LAS alone, it was deemed acceptable for this work. Subsequent experiments with additives produced results where the diffracted X-rays appeared in the same area as the scattering caused by the carbon-fibre capillary.

Despite using a standard exposure time for experiments with the same sample materials, the intensity of the scattered X-rays varied. This seemed to be affected mostly by slight variations in the position of the X-ray beam path through the capillary and can be attributed to the different amounts of sample (and hence,
electrons) exposed to the X-rays. As it was extremely difficult to keep the X-ray beam path through the capillary consistent between experiments, it was not possible to compare the absolute intensity of the scattered X-rays between experiments. This also meant that the contribution of scattering from the carbon-fibre capillary could not be reliably subtracted from results.

3.3.1.2 Analysis of X-ray Diffraction Data

X-ray scattering data were typically collected for 300 s and a two-dimensional scattering pattern obtained; an example is shown in Figure 3.4 (a) for high-active LAS at 60 °C and a static pressure of 4 bar. A dark shadow due to the beam-stop is at the centre of the image and a central region of scatter from the direct beam occurs directly around the beam-stop. Scattering due to the sample is shown by a bright Bragg diffraction ‘ring’. In Figure 3.4 (a), rather than a ring of even intensity, the X-ray scattering is confined to the equatorial position; this will be discussed further in the section on orientation profiles following the section on diffraction profiles.

The ‘raw’ data were corrected for the spherical distortion of the detector surface and analysed using SAXS-online software (Bruker AXS, Madison, USA), which was supplied with the detector. Diffraction or orientation profiles of the scattered X-rays could then be obtained, depending on whether the diffraction data were integrated with respect to the diffraction angle $2\theta$, or azimuthal angle $\chi$ (these angles are defined in Figure 3.2 (d)). The data were then examined with an analytical package ‘DIFFRAC-plus’ (obtained from Bruker AXS, Madison, USA) and Microsoft Excel.

Diffraction Profiles (Intensity versus Diffraction Angle, 2\theta)

Diffraction profiles are plots of scattered X-ray intensity (I) versus diffraction angle ($2\theta$). These plots were obtained by integrating the ‘raw’ scattering pattern from 0 to 180° $\chi$ for all values of $2\theta$, using a step size of $2\theta = 0.01^\circ$. From the diffraction profiles, peaks of scattered X-ray intensity can be detected; these correspond to the diffraction ‘rings’ present in the scattering pattern. The peaks occur at particular values of $2\theta$ related to the length of the regular repeating units in the sample’s microstructure by the Bragg equation (Appendix C).
A diffraction profile for high-active LAS at 60 °C and a static pressure of 4 bar is shown in Figure 3.4 (b). The maximum scattered intensity occurs at 2θ ~ ca. 2.95°, which corresponds to the lamellar bilayer repeat distance of ca. 30 Å. This was also seen previously by McKeown (2001) who found that this prominent peak really consisted of several closely-spaced adjacent peaks. Factors that could have contributed to the poor resolution of the adjacent peaks were the use of an X-ray beam with relatively large cross-sectional area (thus limiting the resolution), and the thickness of the sample. In that study it was also found that a greater resolution of peaks was achieved when the X-ray beam path was directed to the side rather than the centre of the capillary. This was attributed to the effectively narrower beam going through the capillary itself and the thinner sample in this region.

In the present work, the position of the X-ray beam through the capillary proved difficult to control. Thus the results presented in the following chapters are obtained from experiments with the X-ray beam at varying positions relative to the capillary.

◊ Orientation Profiles (Intensity versus Azimuthal Angle, χ)

Orientation profiles are plots of the scattered X-ray intensity (I) versus azimuthal angle (χ). In relation to the scattering patterns obtained from experiments, orientation profiles represent the distribution of scattering intensity about a Bragg diffraction ‘ring’. While the diffraction profiles specify the length of particular repeating units within the sample microstructure, the orientation profiles relate to the orientation of particular repeating units.

Orientation profiles were obtained over an appropriate range of 2θ for all values of χ (i.e. 0 to 360° χ), using a step size of 0.1° χ. The appropriate range of 2θ was chosen to avoid scattering close to the beam-stop and could vary depending on the raw scattering pattern obtained from experiments. Values of 2θ were chosen to correspond to values of 2θ where peaks of scattered intensity occurred in the diffraction profile. Although the diffraction profiles for high-active LAS processed with different additives varied, the usual range for integration was from 2θ = 2.6 – 3.3°. In some cases however, scattering from the sample would also occur at smaller angles (typically 2θ = 1.3 – 2.1°). This scattering region
appeared closer to the beam-stop where interference from scattering due to the carbon-fibre capillary was unavoidable.

It is useful to define terms used in relation to orientation profiles. An increase in scattering intensity at both $\chi = 90^\circ$ and $\chi = 270^\circ$ is referred to as the *equator*. When scattered intensity peaks occur at both $\chi = 0^\circ$ and $\chi = 180^\circ$, this is referred to as the *meridian*. Scattering that is more intense at the equator or meridian corresponds to a preferred orientation of microstructures within the sample, whereas an even distribution of diffracted X-rays for all values of $\chi$ indicates that there is no preferred orientation. In the orientation profile illustrated in Figure 3.4 (c), high-active LAS at 60 °C at a static pressure of 4 bar is shown to have a definite alignment of microstructure. This ordered arrangement of lamellar bilayers is likely to have resulted from loading the sample into the capillary (McKeown, 2001).

### 3.3.2 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a technique for investigating the microstructure of material and is complementary to X-ray scattering methods. The SEM technique involves an electron beam scanning the surface of the sample; secondary electrons from the atoms on the surface are ejected by interactions with the primary electrons of the beam, and are collected to form an image of the sample topography.

#### 3.3.2.1 Cryogenic Preparation of Samples

Conventional SEM requires the sample to be exposed to a high vacuum. This is a distinct disadvantage for samples that contain water. Despite this, SEM techniques are popular in areas such as food science, where samples generally contain considerable water, due to methods for the cryogenic preparation of samples. The goal of cryogenic preparation is to freeze all the available water in the sample as rapidly as possible in order to minimise the size of the ice crystals that form during this process, thus minimising disruption of the sample microstructure (Aguilera and Stanley, 1999). Throughout this work, cryogenic
preparation was used to enable cryo-SEM observations of LAS-based samples processed with various additives.

3.3.2.2  Cryo-SEM Equipment and Procedure

Cryo-SEM observations could only be made after paste extrudate samples had been removed from the MPR capillary assembly after shearing. Due to the limited availability of cryo-SEM equipment, extrudate samples were first stored in sealed vials at ca. 18 °C, before cryo-SEM observations were made, typically the delay was between one and eight days. The microstructural features of the processed paste appeared to be largely intact despite the delay, however ‘aging’ effects were seen in some cases (further discussion on the stability of shear-induced microstructures will follow in Chapter 6).

For this work, a Philips XL30 FEG (Fei Company, Oregon, USA) scanning electron microscope was used; this was located in the Multi-Imaging Centre, University of Cambridge. A portion of extrudate sample was clamped onto the cryo-SEM sample holder with its circular cross-section exposed and glue applied around the sample to help fix it in place. The sample holder was attached to a transfer rod, and immersed into ‘slushy’ nitrogen at –210 °C for rapid freezing. A vacuum was created to prevent water from condensing, and the sample holder transferred by an airlock to a ‘cryo-prep’ chamber controlled by a CT 1500 cold stage controller (Oxford Instruments, UK). A scalpel blade was then used to induce fracturing of the frozen extrudate by tapping the sample with the blade; this was carried out under vacuum (10⁻⁶ mbar) at –120 °C to give clean fracture surfaces. Following this, the fracture surface was coated with a gold/palladium alloy in the presence of argon (ca. 2 mbar) to form a metal layer ca. 5 nm thick. The sample holder was then transferred through a gate valve to the microscope chamber, and placed on the cryo-stage. Cryo-SEM images were then obtained at –150 °C and 10⁻⁶ mbar.

3.3.2.3  Analysis of Cryo-SEM Images

The cryo-SEM images were captured digitally with Oxford Instruments software (XL Microscope Control for XL Microscopes, Version 5.39) and saved as grayscale images using Microsoft Adobe Photoshop software. Some of the
processed LAS-based samples possessed microstructures that were suitable for quantitative image analysis; these microstructures consisted of tightly packed spherical structures (Multi-Lamellar Vesicles or MLVs – further discussion will follow in subsequent chapters). For these samples, the size distribution of MLVs could be obtained using Image Tool software (UTHSCSA, Version 3.00 for Windows) to analyse images. Typically, over one hundred MLVs were measured per image to get a representative sample of MLVs within the paste material, though this varied depending on the number of distinct MLVs appearing in each image. As the contrast of individual MLVs in the digital images was poor, the ‘pencil’ tool in Adobe Photoshop was used to mark the size of each MLV before the Image Tool software was used for analysis.

### 3.4 Overall Experimental Procedure

In the previous sections, descriptions of the materials, processing equipment and characterisation techniques used for the current work were presented. The purpose of this section is to describe the overall experimental procedure, particularly the sample loading procedure used for the MPR. It was necessary to establish a sample loading protocol for experiments, as the reproducibility of experiments with lyotropic liquid crystalline systems such as high-active LAS can be affected (McKeown, 2001).

A description of the overall experimental procedure typically followed is presented below.

1. The MPR and the X-ray cabinet were coupled together and the sample-detector distance calibrated using a silver behenate standard.
2. The three sections of the MPR (with the pistons and X-ray inserts in place) were connected to the heating circuit (Figure 3.1) and preheated to the desired temperature for shearing experiments. A thermocouple was used in the central section to monitor the temperature in the system.
3. Using a spatula, additives (selected from Table 3.2) were then gently ‘pre-mixed’ into 20 g of high-active LAS paste; the ‘quiescent’ paste had been stored in a sealed container at ca. 18 °C prior to experiments. As this pre-
mixing step inevitably subjected the LAS paste to some amount shear, experiments involving high-active LAS only (without additives) also used the spatula to ‘mix’ the paste for consistency in sample preparation.

iv) Section 3 of the MPR assembly (Figure 3.1) was removed from the heating circuit. Some of the ‘mixed’ paste was then loaded into the section with a spatula, filling the section by pushing material from the bottom end of the barrel to the top. Section 3 was placed back into the MPR onto the lower piston, excess sample removed from the top and an o-ring seal fitted.

v) The capillary assembly inserts were removed from section 2 of the MPR and paste was loaded into them (Figure 3.1). This was achieved by pushing the paste from one end of an insert to the other end by hand. The carbon-fibre capillary insert was filled in a similar manner and then fitted in between the two longer inserts, with seals placed between each insert. The conical sections at the ends of the longer capillary inserts were also filled level with paste. The complete capillary assembly was then fitted back into section 2 of the MPR and an o-ring seal put in place.

vi) With the three sections arranged on top of each other back in the MPR, the MPR software was used to move the platform towards section 1, pushing the sections together, thus closing the system. For each experiment, approximately 17 g of sample material was loaded into the MPR system.

vii) A check was then carried out to ensure that the X-ray beam path could pass through the sample to the X-ray detector. Where necessary, section 2 of the MPR was rotated slightly to allow the beam to pass through the capillary. The table on which the X-ray unit was fixed also allowed some adjustment of the X-ray path relative to the sample.

viii) The pressure transducers were ‘re-zeroed’ to 1 bar using the MPR software. A vacuum pump was used to remove air in the system and the upper piston moved down 22.5 mm from the uppermost position using the ‘move pistons’ function on the MPR software interface. This allowed the vacuum to be maintained.
The system was then left for at least 45 minutes to allow the sample to equilibriate to the experimental temperature required.

The ‘pressure control’ function on the MPR software interface was used to move the pistons and to compress the sample. The bottom piston was first moved upwards at \( \text{ca. } 0.06 \, \text{mm s}^{-1} \) and the upper piston moved downwards until a static pressure of 4 bar was obtained with \( P_t \) and \( P_b \) constant.

A freshly filled helium tube was put in place between the MPR and the detector.

An X-ray image of the compressed sample was then taken to determine the initial microstructural state of the sample (prior to shearing).

Following this, the experiment was carried out in multi-pass mode (Section 3.2.2.3), and the sample sheared for the required duration. At intervals throughout the experiment, pressure data and X-ray scattering images were collected (Section 3.2.3.2 and Section 3.3.1.2).

After the sample had been sheared for the required time, the capillary inserts were removed from the MPR. A 2 mm diameter brass rod was then used to carefully push the paste extrudate from the capillary. The extrudate samples were stored in sealed plastic vials at \( \text{ca. } 18 ^\circ \text{C} \) until cryo-SEM observations could be made (Section 3.3.2).

Due to difficulties in standardising the ‘pre-mixing’ stage required to distribute the additives in the high-active LAS prior to shearing in the MPR, some variation in the state of paste samples immediately prior to shearing was unavoidable. Inevitably this resulted in some variation of the pressure and microstructural data obtained under similar experimental conditions. Despite this, useful results were still attained; this will be discussed further when results are presented in following chapters.

### 3.5 Summary

This chapter has described the materials, equipment and experimental techniques used throughout this study. In this work, a novel processing device (the MPR)
was used for shearing the sample material in addition to monitoring its rheological behaviour. The X-ray unit attached to the MPR enabled \textit{in-situ} microstructural measurements to be made during the shearing process. After the sample material had been sheared, cryo-SEM observations were made of the resultant extrudate, complementing the X-ray scattering technique. As high-active LAS is a system that is sensitive to variations in experimental procedure, a well-defined protocol had to be established. This enabled the comparison of results from experiments investigating the effect of different additives on the processing behaviour and microstructure of high-active LAS.
Table 3.1. Typical composition of industrial high-active LAS. Two batches manufactured by the same route are shown for comparison. The final neutralisation step with concentrated caustic soda was carried out for Batch 1 by Manro Performance Chemicals (Stalybridge, England) and in-house at Procter & Gamble (Dartford Technical Centre, England) for Batch 2. Taken from McKeown (2001).

<table>
<thead>
<tr>
<th></th>
<th>Batch 1</th>
<th>Batch 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Analytical Data (wt. %)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Active matter</td>
<td>76.4</td>
<td>77.2</td>
</tr>
<tr>
<td>H₂O (Water)</td>
<td>20.08</td>
<td>19.10</td>
</tr>
<tr>
<td>LAB (Linear alkylbenzene)</td>
<td>1.69</td>
<td>1.65</td>
</tr>
<tr>
<td>Na₂SO₄ (Sodium sulfate)</td>
<td>0.64</td>
<td>0.42</td>
</tr>
<tr>
<td>NaOH (Sodium hydroxide)</td>
<td>0.13</td>
<td>0.37</td>
</tr>
<tr>
<td>NaCl (Sodium chloride)</td>
<td>0.01</td>
<td>0.16</td>
</tr>
<tr>
<td>Molecular weight of LAB (g mol⁻¹)</td>
<td>240.7</td>
<td>240.3</td>
</tr>
<tr>
<td><strong>Alkyl Chain Distribution Data (wt. %)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt; Linear C₁₀</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>Linear C₁₀</td>
<td>10.7</td>
<td>10.9</td>
</tr>
<tr>
<td>Linear C₁₁</td>
<td>34.8</td>
<td>31.3</td>
</tr>
<tr>
<td>Linear C₁₂</td>
<td>29.4</td>
<td>31.0</td>
</tr>
<tr>
<td>Linear C₁₃</td>
<td>18.6</td>
<td>19.8</td>
</tr>
<tr>
<td>Linear C₁₄</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>&gt; C₁₄</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Tetrалins and complex hydrocarbons including branched material</td>
<td>5.5</td>
<td>6.0</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>of which 2-phenyl isomer content</td>
<td>18.3</td>
<td>18.4</td>
</tr>
</tbody>
</table>

Data were obtained using standard analytical methods by Mr. John Grey (Procter & Gamble, Newcastle Technical Centre, England)
Table 3.2. List of salts and the amount used with high-active LAS. Where different amounts were used in experiments, these will be stated in the text.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Molecular formula</th>
<th>Weight used (g/20g of LAS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium chloride*</td>
<td>NH₄Cl</td>
<td>1.8</td>
</tr>
<tr>
<td>Potassium chloride§</td>
<td>KCl</td>
<td>2.5</td>
</tr>
<tr>
<td>Sodium chloride*</td>
<td>NaCl</td>
<td>2.0</td>
</tr>
<tr>
<td>Sodium citrate (dihydrate)*</td>
<td>Na₂C₆H₅O₇•2H₂O</td>
<td>3.3</td>
</tr>
<tr>
<td>Sodium disilicate “Pyramid P70”¢</td>
<td>Na₂O:2SiO₂</td>
<td>2.0</td>
</tr>
<tr>
<td>Sodium nitrate*</td>
<td>NaNO₃</td>
<td>2.9</td>
</tr>
<tr>
<td>Sodium phosphate monobasic monohydrate*</td>
<td>HNaO₄P•H₂O</td>
<td>4.7</td>
</tr>
<tr>
<td>Sodium phosphate tribasic dodecahydrate*</td>
<td>Na₃O₄P•12H₂O</td>
<td>4.3</td>
</tr>
<tr>
<td>Sodium sulfate (anhydrous)*</td>
<td>Na₂SO₄</td>
<td>2.4</td>
</tr>
<tr>
<td>Sodium sulfite (anhydrous)*</td>
<td>Na₂O₃S</td>
<td>2.1</td>
</tr>
<tr>
<td>Tetramethylammonium chloride*</td>
<td>C₄H₁₂ClN</td>
<td>3.7</td>
</tr>
<tr>
<td>Tetramethylammonium nitrate*</td>
<td>C₄H₁₂N₂O₃</td>
<td>4.6</td>
</tr>
</tbody>
</table>

* Supplied by Fisher Scientific, UK.
# Supplied by BDH, UK.
§ Supplied by Merck, EU.
¢ Supplied by INEOS Silicas, Netherlands.

Table 3.3. Scope of MPR processing parameters. After McKeown (2001).

<table>
<thead>
<tr>
<th>MPR (version III)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Barrel internal diameter</td>
<td>15 mm</td>
</tr>
<tr>
<td>Test piece geometry</td>
<td></td>
</tr>
<tr>
<td>Capillary internal diameter (nominal)</td>
<td>1, 2, 4 mm</td>
</tr>
<tr>
<td>Capillary length (nominal)</td>
<td>10, 20, 40, 90 mm</td>
</tr>
<tr>
<td>Slit length, depth, width (nominal)</td>
<td>10 mm × 10 mm × 1 mm</td>
</tr>
<tr>
<td>Piston speed</td>
<td>0.05 - 300 mm s⁻¹</td>
</tr>
<tr>
<td>Maximum piston stroke</td>
<td>15 mm</td>
</tr>
<tr>
<td>Minimum piston stroke</td>
<td>0.05 mm</td>
</tr>
<tr>
<td>Temperature</td>
<td>15 - 200 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>0.01 - 20 MPa (gauge)</td>
</tr>
<tr>
<td>Volumetric flow rate</td>
<td>0 - 5 × 10⁻⁵ m³ s⁻¹</td>
</tr>
</tbody>
</table>
Figure 3.1. Schematic diagram of the ‘Multi-Pass Rheometer (MPR) version III’ with X-ray capillary assembly in the central section. After McKeown (2001).
Figure 3.2. Photographs (a to c) and a schematic diagram (d) showing the layout of the Cambridge MPR with attached X-ray unit. After McKeown (2001).
Figure 3.3. Typical MPR results for high-active LAS sheared in multi-pass mode at 60 °C using standard MPR processing parameters. Results are plotted with the corresponding position of the bottom piston: (a) top and bottom pressure transducer readings are shown; (b) the calculated pressure difference, $\Delta P$, is shown with the pseudo-steady state pressure, $\Delta P_p$, which can be obtained from $2\Delta P_p$ marked on the graph.
Figure 3.4. X-ray diffraction results obtained from high-active LAS at 60 °C, compressed to a static pressure of 4 bar, in the MPR. The following types of results are shown: (a) X-ray scattering pattern, where the scattering due to the carbon-fibre capillary is shown within the dotted green boundary, (b) diffraction profile and (c) orientation profile.
Chapter 4

SODIUM DISILICATE - AN INDUSTRIAL STRUCTURING AGENT

In Section 1.4, a description of the industrial paste-structuring process was presented; high-active LAS and sodium disilicate powder are forced through a twin-screw extruder at 60 °C and the resultant paste appears firm and ‘structured’. Work by McKeown (2001) showed that structured LAS paste could also be obtained at particular shear rates when LAS paste was processed (without additives) at 25 °C, though this did not occur at 60 °C. The structured paste possessed a tightly-packed MLV microstructure rather than the planar bilayer microstructure found in unprocessed LAS paste.

The current chapter will use this work by McKeown (2001) as a basis for studying the paste-structuring process. Its purpose is to examine, at different temperatures, the paste-structuring of high-active LAS with sodium disilicate, the additive used in industry. The microstructure and processing behaviour of LAS paste structured with sodium disilicate will be compared with LAS paste structured in the absence of structuring agents.

4.1 Experimental Description

Detailed descriptions of the materials, equipment, experimental protocol and characterisation techniques used for these experiments are given in Chapter 3. In the present chapter, results from experiments with sodium disilicate and high-active LAS will be described and compared with results obtained from high-active LAS alone.
4.1.1 Materials and Methods

High-active LAS and colloidal sodium disilicate powder were used for the experiments. These are described in Section 3.1. The amount of sodium disilicate processed with the LAS paste was kept constant throughout the experiments at 10 wt. %.

The processing of materials was carried out in the MPR at 25, 40, 60 and 75 °C using the standard processing parameters given in Section 3.2.2.3. Rheological and X-ray scattering data were obtained from the MPR with attached X-ray unit and cryo-SEM observations were also made using the resultant extrudate.

4.2 Results and Discussion

The results and discussion section has been divided into two main subsections. These subsections correspond to groups of experiments that have been conducted to examine: (1) the effect of temperature on high-active LAS during shear without sodium disilicate and (2) the effect of temperature on high-active LAS during shear with sodium disilicate.

4.2.1 Effect of Temperature on High-Active LAS During Shear: without Sodium Disilicate

Although McKeown (2001) studied the effect of temperature on high-active LAS during shear in the absence of structuring agents, only two temperatures were examined: 25 °C and 60 °C. In this section, results will be presented from experiments repeated at these temperatures with the batch of LAS used in this work. Results from experiments at 40 °C and 75 °C will also be included.

4.2.1.1 Rheological Results from the MPR

Typical rheological results obtained from shearing high-active LAS in the MPR using standard processing parameters at different temperatures (25, 40, 60 and 75 °C) are shown in Figure 4.1, where the pseudo-steady state pressure, \( \Delta P_p \), is plotted against processing time. In all the experiments shear was applied for 60 minutes apart from the experiment conducted at 60 °C, in which shear was for 30 minutes; this was considered sufficient for high-active LAS to reach rheological
steady state in the experiments carried out by McKeown (2001). Due to the pre-mixing stage in the experimental loading procedure (Section 3.4), some variation in the initial state of samples prior to shear was unavoidable, however experiments have been repeated several times and reproducible trends demonstrated. Values of $\Delta P_p$ for repeated experiments were compared after 60 minutes of shear and the 90% confidence intervals were calculated using the Student’s $t$-distribution; these are plotted in Figure 4.1.

The results in Figure 4.1 show that the high-active LAS reaches rheological steady state ($\Delta P_p$ remaining constant with shear) when sheared at all the temperatures investigated. A period of rheopectic behaviour (where viscosity increases with time at a given shear rate) is exhibited by high-active LAS at 25 °C. This rheopectic region is not seen for samples processed at 40, 60 or 75 °C, even when more data points (obtained immediately after the commencement of shear) are included in the results. At both 25 °C and 40 °C, there is a region of slight thixotropy (where viscosity decreases with time at a given shear rate) before steady state is achieved; this is more pronounced at 25 °C than at 40 °C. The thixotropic region is not present at the higher temperatures of 60 °C and 75 °C and steady state is achieved immediately with shear.

From the 90% confidence intervals for $\Delta P_p$ at steady state, it is evident that the process temperature has a significant effect on the magnitude of $\Delta P_p$. For example, processing high-active LAS at 25 °C results in a steady state $\Delta P_p$ value of 60 ± 3 bar while at 40 °C the corresponding value is less than half at 22 ± 4 bar. At 60 °C and 75 °C the steady state values of $\Delta P_p$ are not significantly different from each other (both at ca. 6 bar) but are much lower than at 40 °C. The higher values of $\Delta P_p$ at 25 °C indicate that the samples have an increased resistance to flow (increased viscosity) and qualitatively these samples appear to be ‘structured’.

When the rheological results obtained from shearing high-active LAS at 25 °C are compared with the results from McKeown (2001) where the same shearing parameters were used, slight differences are detected. In the previous work at 25 °C, rheopectic behaviour (where $\Delta P_p$ increases as the sample is sheared) was initially observed to a maximum of ca. 90 bar. This was followed by thixotropic
behaviour (where $\Delta P_p$ decreases as the sample is sheared) to ca. 70 bar and then weakly rheopectic behaviour to ca. 80 bar after 60 minutes of shear. The weakly rheopectic (rather than steady state behaviour) and higher magnitude values of $\Delta P_p$ seen by McKeown (2001) are likely due to slight differences in the sample loading procedure (particularly the pre-mixing stage) and also in the composition of the particular high-active LAS batch used. At 60 °C however, the rheological results are in good agreement.

4.2.1.2 X-ray Diffraction Results

In addition to the rheological results obtained during the shearing experiments conducted on high-active LAS, X-ray diffraction data were also collected. The orientation profiles obtained from the X-ray scattering patterns will be examined, followed by a discussion of data relating to the d-spacing (or length of the regular repeating unit) within the sample microstructure.

◊ Orientation of Microstructure

In Figure 4.2, orientation graphs of high-active LAS samples are shown: (a) compressed to a static pressure of 4 bar prior to shearing and (b) after 20 minutes of shearing. The graphs compare orientation profiles (where X-ray intensity is plotted in arbitrary units against the azimuthal angle, $\chi$) for samples at temperatures of 25, 40, 60 and 75 °C at similar points during the experiment. From Figure 4.2 (a), the initial state of the compressed samples prior to shear is fairly similar at the different temperatures. The peaks of X-ray intensity at $\chi \sim 90^\circ$ and $270^\circ$, indicate that microstructure of the samples is oriented, this corresponds to the behaviour reported by McKeown (2001), where the planar bilayers of high-active LAS were thought to be aligned parallel to the plane of the capillary wall. It is interesting to note that at the lower temperatures (25 °C and 40 °C), the peaks of X-ray intensity are slightly skew and not completely centred at $\chi = 90^\circ$ and $270^\circ$. This implies that the compressed samples at these temperatures are not as well-aligned with the capillary as those at 60 °C and 75 °C. After 20 minutes of shear (Figure 4.2 (b)), the orientation profiles for high-active LAS at 60 °C and 75 °C remain unchanged. However at 40 °C, the peaks of X-ray intensity appear more centred at $\chi = 90^\circ$ and $270^\circ$ due to a slight shift of the peaks from the compressed state, implying that with shear the sample
microstructure is aligned to a greater degree. At 25 °C, the fairly even distribution of X-ray intensity for all values of χ corresponds to a change in the microstructure of the sample from an oriented texture to one where there is no preferential orientation of bilayers; this behaviour was also observed by McKeown (2001).

Similar data to that shown in Figure 4.2 are plotted in Figure 4.3. The difference is that the graphs are organised according to the process temperature and that the orientation profiles obtained at various times throughout the shearing experiments are plotted on individual graphs. Each graph displays orientation profiles obtained during sample compression to 4 bar (immediately prior to shearing) and then from 0, 20 and 50 minutes after shearing commenced, although the orientation profile at 50 minutes is not available for the sample at processed at 60 °C. The orientation profiles (plotted as continuous lines) have been shifted along the y-axis for visual clarity. As discussed in Section 3.3.1.1, variations in the scattered intensity between experiments are likely due to slight differences of the X-ray beam position relative to the capillary.

At 25 °C (Figure 4.3 (a)), a change in the microstructure of the high-active LAS occurs as the sample is sheared. When the sample is compressed (prior to shear) an increase in intensity at χ = 90° and 270° indicates the microstructure within the sample is in an oriented state. However, once shear is commenced the intensity is fairly evenly distributed for all values of χ, corresponding to a change from an aligned planar state to an MLV-rich microstructure, also seen by McKeown (2001); during the rest of the shearing process, the orientation profile remains unchanged. The transformation to the MLV-rich microstructure occurs rapidly with shear. Unfortunately the 300 s required to collect each X-ray diffraction pattern (and hence orientation profile) precludes detailed study of the kinetics of this process. For processed high-active LAS at 40, 60 and 75 °C (Figures 4.3 (b), (c), and (d) respectively), orientation profiles with increased scattered intensity at χ = 90° and 270° occur even after shearing for 20 and 50 minutes. This indicates that at these temperatures, strong alignment of planar layers in the sample microstructure persists throughout shear.
Chapter 4: Sodium Disilicate - an Industrial Structuring Agent

◊ Length of the Characteristic Repeating Microstructure Unit (d-spacing)

From X-ray diffraction profiles (i.e. plots of X-ray intensity versus scattering angle, 2θ, as discussed in Section 3.3.1.2) the peaks of X-ray intensity that occur at certain values of 2θ are related to the length of the characteristic repeating unit (or d-spacing) within the sample microstructure by Bragg’s Law (Appendix C, Equation C.7). For the experiments described in this chapter, the d-spacing results obtained at steady state (where the d-spacing remains constant over time at a given shear rate) have been summarised in Figure 4.4. From repeated experiments, 90% confidence intervals for the d-spacing values were calculated using the Student’s t-distribution. From the graph, it is clear that high-active LAS sheared without sodium disilicate possesses a bilayer distance of ca. 30 Å and that the different process temperatures do not produce significantly different results at the 90% confidence level. This is consistent with what McKeown (2001) observed at process temperatures of 25°C and 60°C.

4.2.1.3 Cryo-SEM Results

The cryo-SEM images of high-active LAS sheared at 25, 40, 60 and 75°C are shown in Figure 4.5. Samples were sheared to what was considered rheological steady state: 60 minutes in all cases except for the sample processed at 60°C, which was sheared for 30 minutes. From Figure 4.5 (a), it is evident that the material processed at 25°C possesses a microstructure consisting of densely-packed MLVs of ca. 700 nm diameter; this is consistent with the orientation profiles in Figure 4.3 (a). McKeown (2001) obtained similar findings, although the MLV diameter was reported as ca. 350 nm. In contrast to this, the cryo-SEM images taken of high-active LAS processed at 40, 60 and 75°C (Figure 4.3 (b), (c) and (d) respectively) possess different microstructures to the material processed at 25°C. On closer inspection, the sample processed at 40°C appears to possess a texture in which MLV-like structures are present, though they are not as distinct as the MLVs present at 25°C. At 60°C and 75°C, it is difficult to identify particular structures present in the samples, although there is some indication that a few MLVs could be present. However it is evident that for samples processed at 40, 60 and 75°C the MLV-like structures, if present, do not form the same densely-packed arrangements found in LAS processed at 25°C. It
is likely that at these elevated temperatures the microstructure of the LAS samples consists largely of oriented planar lamellar bilayers coexisting with occasional MLV-like microstructures; this will be considered further in the following discussion section.

4.2.1.4 Discussion

The rheological and microstructural data from experiments in the MPR provide a good basis for understanding the behaviour of high-active LAS when sheared. For LAS processed at 25 °C, the formation of MLVs with shear is consistent with the rheopectic behaviour exhibited. This agrees not only with the trends observed by McKeown (2001) for a different batch of high-active LAS, but also with literature relating rheopectic behaviour to the shear-induced formation of MLVs in other systems (Bergenholtz and Wagner, 1996; Läuger et al., 1996). In comparison to the results obtained in the present work, it is likely that the higher magnitude values of $\Delta P_p$ obtained by McKeown (2001) for similar experiments with high-active LAS at 25 °C are due to the relatively smaller MLV diameters observed in the sample microstructure.

In Figure 4.3 (a), although the orientation profiles for high-active LAS sheared at 25 °C have fairly even distributions of X-ray intensity for values of $\chi$ in comparison with the compressed sample, there are slight increases in intensity occurring at $\chi = 0°, 90°, 180°, 270°$ and $360°$. The slight increase in intensity observed at $\chi = 90°$ and $270°$ can be attributed to aligned planar lamellae coexisting with the MLVs. However, it is not clear if the aligned planar bilayers occur throughout the sample microstructure (this will be further discussed in Chapter 6), if the planar bilayers are confined to the wall of the capillary as observed by McKeown (2001) or if a combination of these factors is present. It is also possible that the increased intensity is caused by distorted MLVs. The slight increase in intensity observed at $\chi = 0°, 180°$, and $360°$ is due to scattering from the carbon-fibre capillary and can also be observed in the orientation profiles obtained from experiments with other paste samples and the standard reference powder sample (silver behenate) used for calibration.
At the processing temperature of 40 °C, the magnitude of $\Delta P_p$ values with shear appear intermediate between the results obtained from experiments conducted at 25 °C and the elevated temperatures of 60 °C and 75 °C. When the cryo-SEM images (Figure 4.5) are examined, the results relate well to the rheological response of these materials. The highest values of $\Delta P_p$ at rheological steady state are exhibited for high-active LAS sheared at 25 °C, which possesses a densely-packed MLV microstructure. At 40 °C, the intermediate values of $\Delta P_p$ that are obtained correspond to the less distinct texture of MLVs that are observed, coexisting with planar lamellae, while at 60 °C and 75 °C, the small values of $\Delta P_p$ relate to the largely planar lamellar microstructure that exists. The orientation profiles (Figure 4.3) do not appear to be sensitive to the ‘non-distinct’ MLVs that form at 40, 60 and 75 °C; this reflects the microstructure being mostly in the planar form. Although the orientation profiles at 40 °C do not exhibit the significant reduction in peak intensity with shear that is observed at 25 °C (Figure 4.3 (a) and (b)), some microstructural change does occur with shear; this is evident as there is some difference between the orientation profiles for compressed and sheared samples.

The immediate rheological steady state achieved with LAS samples sheared at 60 °C and 75 °C (Figure 4.1) implies that the microstructure of the samples also reaches a steady state very rapidly: this is confirmed by the orientation profiles of sheared samples that remain unchanged over the processing time (Figure 4.3 (c) and (d)). It is therefore possible that the MLV-like structures, observable in the cryo-SEM images of these samples, form during the pre-mixing stage which is part of the sample loading process for all experiments and involves some shearing of samples with a spatula at room temperature. This is a reasonable assumption: from preliminary experiments at similar temperatures using a Kenwood food processor to apply shear, samples of high-active LAS have been observed to form MLVs. After the pre-mixing stage, the samples are heated to the processing temperature used for shearing in the MPR. At the elevated temperatures of 60 °C and 75 °C, it is probable that the density of defects in the samples is reduced and that further MLVs do not form as a rich defect texture is thought necessary for this (McKeown, 2001; Diat and Roux, 1993; Zipfel et al., 1999). The microstructure of high-active LAS with shear at elevated
temperatures consists largely of planar lamellar bilayers that align with shear (from the evidence presented in the orientation profiles) coexisting with a relatively small number of MLV-like microstructures.

4.2.2 Effect of Temperature on High-Active LAS During Shear: with Sodium Disilicate

Having examined the effect of temperature on high-active LAS during shear in the absence of structuring agents, the focus will now be to investigate the effect of adding sodium disilicate powder (an industrial structuring agent) to high-active LAS. In the experiments presented in this section, 10 wt. % sodium disilicate was sheared with high-active LAS using standard MPR processing parameters at process temperatures of 25, 40, 60 and 75 ºC.

4.2.2.1 Rheological Results from the MPR

In Figure 4.6, typical rheological results are shown for high-active LAS sheared with 10 wt. % sodium disilicate using standard MPR processing parameters at various process temperatures. As in Figure 4.1, the pseudo-steady state pressure, \( \Delta P_p \), is plotted against processing time and 90 % confidence intervals for \( \Delta P_p \) (calculated using the Student’s \( t \)-distribution) are shown at 60 minutes of shear.

From Figure 4.6, it is evident that when shear is first applied high-active LAS exhibits rheopectic behaviour. After 60 minutes of shear, samples at 25 ºC and 40 ºC continue to be weakly rheopectic whereas those at 60 ºC and 75 ºC come to an apparent rheological steady state. Repeated experiments have shown similar trends and further experiments have shown that the weakly rheopectic behaviour can persist after 60 minutes of processing. It is not clear why the samples processed at cooler temperatures should be weakly rheopectic while samples at higher temperatures reach steady state. From the 90 % confidence intervals for \( \Delta P_p \) after 60 minutes of shear, it is evident that there is no significant difference in the magnitude of \( \Delta P_p \) (ca. 85 bar) between the samples processed at various temperatures. This is a considerably different scenario to that presented in Figure 4.1 where the results are shown for LAS processed without sodium disilicate. When the results are compared between Figure 4.1 and Figure 4.6, it is also apparent that LAS processed with sodium disilicate consistently exhibits higher values of \( \Delta P_p \) for corresponding process temperatures and these can be
several times higher for pastes processed at elevated temperatures (40 to 75 °C). When the pastes processed with sodium disilicate were examined after shearing, they appeared qualitatively to be ‘structured’.

### 4.2.2.2 X-ray Diffraction Results

◊ Orientation of Microstructure

In Figure 4.7, equivalent graphs to those displayed in Figure 4.2 are shown, illustrating typical results obtained from high-active LAS with sodium disilicate (a) compressed to a static pressure of 4 bar and (b) after 30 minutes of shearing. Orientation profiles (where X-ray intensity is plotted in arbitrary units against the azimuthal angle, $\chi$) are compared for samples at temperatures of 25, 40, 60 and 75 °C; for visual clarity, the orientation profiles have been shifted along the y-axis and are plotted as continuous lines.

Figure 4.7 (a) illustrates the microstructure of samples prior to shear. It is evident that for the samples at 25, 40 and 60 °C, the sample preparation and loading procedures have resulted in samples that possess a different microstructural state to those in Figure 4.2, though the microstructure of the compressed sample at 75 °C is similar in both cases. In the orientation profiles for samples at 25, 40 and 60 °C the distribution of X-ray intensity is fairly even for all values of $\chi$, though slight peaks at $\chi \sim 90^\circ$ and $270^\circ$ can still be detected; it is likely that these orientation profiles are due to MLV-rich microstructures formed during the pre-mixing process. The differences between the orientation profiles in Figure 4.7 (a) can be attributed to the inherent variation present in the pre-mixing and sample loading processes.

The change in sample microstructure for high-active LAS samples processed with sodium disilicate after 30 minutes of shearing in the MPR, is shown in Figure 4.7 (b). From the initial compressed state of the samples in Figure 4.7 (a), it is evident that with shear, there has been some change in the microstructure of the samples. This change is clearest for samples at 60 °C and 75 °C where after 30 minutes of shear the orientation profiles are much flatter than in Figure 4.7 (a). For samples processed at 25 °C and 40 °C, the orientation profiles obtained after 30 minutes shear still retain slight peaks at $\chi \sim 90^\circ$ and $270^\circ$. At 40 °C there is a
slight shift in the peak positions with shear, however at 25 °C there does not appear to be a difference in the orientation profile with shear. The relatively flat orientation profiles obtained for all samples after 30 minutes shear correspond to MLV microstructures being present in the paste; further evidence will be presented in Section 4.2.2.3.

In Figure 4.8, the orientation profiles obtained throughout shearing experiments are plotted on graphs corresponding to the different process temperatures. As before, the orientation profiles are shifted along the y-axis and plotted as continuous lines. From this figure, it is apparent that any changes in the orientation of the microstructures occur within 30 minutes of shear and that with further shear, no significant changes are detected.

◊ **Length of the Characteristic Repeating Microstructure Unit (d-spacing)**

The graph shown in Figure 4.4 summarises the d-spacing results obtained from experiments conducted with high-active LAS and sodium disilicate at different process temperatures. The 90 % confidence intervals are also shown from repeated experiments. For all these experiments, the d-spacing measurements in the microstructure of the samples remained constant (at steady state) with shear in the MPR. From the results shown in Figure 4.4, the d-spacing values (corresponding to the bilayer repeat distance) for high-active LAS samples sheared with sodium disilicate appear to be between 29.8 and 29.0 Å, significantly lower than the values observed in the absence of sodium disilicate. The results possibly suggest a downward trend in d-spacing with temperature although for the point at 40 ºC the error bar is too large for this. It is possible that the differences are due to variability in (1) the degree to which the sodium disilicate powder was dispersed throughout the LAS paste and (2) the amount of sample material actually loaded into the MPR system.

4.2.2.3 **Cryo-SEM Results**

In Figure 4.9, cryo-SEM images of high-active LAS sheared for 60 minutes with sodium disilicate at 25, 40, 60 and 70 ºC are shown. It is clear that all the samples possess similar microstructures of densely-packed spherical MLVs, where the MLV diameters range from *ca.* 50 –500 nm. In comparison to the
results shown in Figure 4.5, it is obvious that shearing high-active LAS with sodium disilicate has a significant effect on the sample microstructure, particularly at temperatures above 25 °C. This will be further discussed in the following section.

4.2.2.4 Discussion

The rheological response of high-active samples of LAS sheared with sodium disilicate (Figure 4.6) is significantly different to that displayed for high-active LAS sheared without sodium disilicate (Figure 4.1). At particular process temperatures, higher $\Delta P_p$ values are consistently obtained from samples processed with sodium disilicate. The difference in $\Delta P_p$ values at 25 °C can be related to the difference in the size of MLVs present in the samples. MLVs formed from shearing high-active LAS with sodium disilicate are on average smaller than those formed without sodium disilicate (compare Figure 4.9 (a) with Figure 4.5 (a)); the smaller MLVs result in a larger values of $\Delta P_p$ (i.e. more viscous, ‘stiffer’ pastes). For samples processed at 40, 60 and 75 °C, it is evident that the significantly higher $\Delta P_p$ values that result from shearing with sodium disilicate are due to the densely-packed MLVs present in the paste microstructure rather than the aligned planar bilayers present when sodium disilicate is not used. The difference in the viscosity of these microstructural states was also observed in the AOT/brine system studied by Léon et al., (2000) where at ‘high’ salinity, a high viscosity gel-like MLV phase was formed with shear from a low viscosity planar state.

As discussed in Section 4.2.1.4, the rheoplectic behaviour exhibited by samples processed at all temperatures with sodium disilicate is characteristic of the shear-induced formation of MLVs (McKeown, 2001; Bergenholtz and Wagner, 1996; Läuger et al., 1996). However the rheoplectic response is over a more prolonged period than the rheoplectic behaviour seen for high-active LAS sheared without sodium disilicate. This prolonged rheoplectic response implies that additional changes to the microstructure occur over time with shear. A possible explanation is that the sodium disilicate powder takes time to dissolve into the high-active LAS, gradually affecting the microstructure of the material and giving rise to the sustained rheoplectic behaviour that is observed.
When Figure 4.6 and Figure 4.8 are examined, it is evident that the X-ray diffraction data do not reflect the rheological changes occurring during the weakly rheopectic period for 25 °C and 40 °C (from 30 minutes to 50 minutes of shear). As the orientation profiles and d-spacing values are unchanged during this period of shear, this implies that the rheological changes in this period are not due to large changes in bilayer repeat distance or in the proportion of MLVs to planar bilayers present in the sample. It is reasonable to assume that the rheopectic response is due rather to the effect of shear on whole vesicle shells/bilayers, possibly similar to that observed by Bergmeier et al. (1999), where an increase in shear rate caused vesicle shells to be stripped off the MLVs. The peaks of X-ray intensity that persist in the orientation profiles obtained from samples of high-active LAS sheared with sodium disilicate at 25 °C and 40 °C (Figures 4.8 (a) and (b), respectively) are most likely due to planar lamellae remaining amongst the MLV-rich microstructure, although the cryo-SEM images presented in Figure 4.9 did not show evidence of this. Further discussion of microstructures consisting of planar and vesicular lamellae will be presented with supporting results in Chapter 6.

The significant effects of shearing high-active LAS with sodium disilicate, particularly the induction of MLVs at elevated temperatures, are clear, though the mechanism by which this is achieved is not obvious. Some insight into the mechanism for MLV formation with sodium disilicate can be gleaned from the d-spacing values that are obtained from various samples. Although there is no definite trend in d-spacing values with processing temperature for samples sheared with sodium disilicate, when results at each temperature are compared with those obtained without sodium disilicate, the d-spacing values for samples processed with sodium disilicate are consistently smaller (Figure 4.4). The addition of sodium disilicate therefore has the effect of reducing the bilayer repeat distance in high-active LAS. It is possible that the reduced bilayer repeat distance is necessary for MLVs to form with shear at elevated temperatures; this will be discussed in more depth in Chapter 5. The smaller bilayer repeat distance is likely due to the dissolved sodium disilicate affecting the ionic strength of water within the LAS bilayers which may change the effective head-group size of the LAS molecule or the electrostatic forces within and between layers. In the
system investigated by Bergmeier et al. (1999), an increased charge density within the system also appeared to encourage MLV formation.

4.3 Chapter Summary

In this chapter the effect of sodium disilicate, an industrial structuring agent, on the microstructure and rheological behaviour of high-active LAS with shear was examined at various temperatures. It was found that at elevated temperatures (40, 60 and 75 °C), densely-packed MLV structures formed when high-active LAS was sheared with sodium disilicate; without sodium disilicate the sheared samples possessed a very different microstructure consisting largely of planar bilayers. Paste samples with densely-packed MLV microstructures appeared qualitatively ‘structured’ and to exhibit rheoplectic behaviour with high $\Delta P_\rho$ values. The sodium disilicate reduced the bilayer repeat distance in high-active LAS. It is likely that the effect of the sodium disilicate on the ionic strength of the water within the LAS bilayers contributes to the shear-induced MLV formation at high temperatures.

This chapter has presented evidence for the formation of MLVs in high-active LAS using both an industrial structuring agent and an industrially relevant temperature to form the ‘structured’ paste that is necessary for the manufacture of compact detergent powder. The MLV-microstructure is thus industrially important and further study into possible mechanisms for MLV formation in high-active LAS is valuable in helping to understand the process of paste-structuring. At present as there is no reliable theoretical framework for understanding MLV formation (Marlow and Olmsted, 2002), an experimental approach has been taken in this study where the effect of various salts on the shear-induced microstructures that form in high-active LAS has been investigated. Chapters 5, 6 and 7 in this thesis will further investigate the effect of various salts on the formation of MLVs and other microstructures in high-active LAS.
Figure 4.1. Typical response of high-active LAS sheared alone (without the addition of salts) in the MPR using standard processing parameters at different process temperatures; the pseudo-steady state pressure difference is plotted against processing time. Where possible, the 90 % confidence intervals for \( \Delta P_p \) (calculated using the Student’s \( t \)-distribution) are shown at 60 minutes of processing time.
Figure 4.2. X-ray intensity versus azimuthal angle, $\chi$, for high-active LAS sheared in the MPR using standard processing parameters where data at different processing temperatures are compared. Typical results are shown for samples: (a) compressed to 4 bar prior to shear and (b) after 20 minutes of shear. The data series are plotted as continuous lines for clarity.
Figure 4.3. X-ray intensity versus azimuthal angle, $\chi$, for high-active LAS sheared in the MPR using standard processing parameters, where data prior to shear (i.e. sample compressed to 4 bar) and throughout the shearing process are compared. Typical results are shown for experiments conducted at (a) 25 °C, (b) 40 °C, (c) 60 °C and (d) 75 °C. The data series have been shifted along the y-axis and are plotted as continuous lines for clarity.
Figure 4.4. Steady state X-ray d-spacing values obtained from high-active LAS paste samples during shear in the MPR (standard processing conditions were used). Results are shown for LAS sheared without any additives and also with 10 wt. % sodium disilicate at process temperatures of 25, 40, 60 and 75°C. The 90 % confidence intervals for the X-ray d-spacing values (calculated using the Student’s t-distribution) are shown.
Figure 4.5. Cryo-SEM images are shown for high-active LAS samples after shearing in the MPR (without the addition of salts) for 60 minutes, except for (c), sheared for 30 minutes. Results are for the following processing temperatures: (a) 25 °C, (b) 40 °C, (c) 60 °C and (d) 75 °C.
Figure 4.6. Typical response high-active LAS sheared with 10 wt.% sodium disilicate in the MPR using standard processing parameters at different process temperatures; the pseudo-steady state pressure difference is plotted against processing time. The 90 % confidence intervals for $\Delta P_p$ (calculated using the Student’s $t$-distribution) are shown at 60 minutes of processing time.
Figure 4.7. X-ray intensity versus azimuthal angle, $\chi$, for high-active LAS sheared with 10 wt. % sodium disilicate in the MPR using standard processing parameters where data at different processing temperatures are compared. Typical results are shown for samples: (a) compressed to 4 bar prior to shear and (b) after 30 minutes of shear. The data series have been shifted along the y-axis and are plotted as continuous lines for clarity.
Figure 4.8. X-ray intensity versus azimuthal angle, $\chi$, for high-active LAS sheared with 10 wt. % sodium disilicate in the MPR using standard processing parameters, where data prior to shear (i.e. sample compressed to 4 bar) and throughout the shearing process are compared. Typical results are shown for experiments conducted at (a) 25 °C, (b) 40 °C, (c) 60 °C and (d) 75 °C. The data series have been shifted along the y-axis and are plotted as continuous lines for clarity.
Figure 4.9. Cryo-SEM images are shown for high-active LAS samples sheared in the MPR with 10 wt. % sodium disilicate for 60 minutes. Results are for the following processing temperatures: (a) 25 ºC, (b) 40 ºC, (c) 60 ºC and (d) 75 ºC.
Chapter 5

Further Salts Inducing MLVs with Shear

In Chapter 4, the effect of sodium disilicate on the shear-induced behaviour of high-active LAS was examined at various processing temperatures and compared to the behaviour exhibited by high-active LAS when sheared alone. As an industrial structuring agent, sodium disilicate has been used to ‘structure’ (make firmer) high-active LAS paste at 60 °C in the large-scale production of compact detergent powders by agglomeration. This change in high-active LAS properties has also been observed in MPR experiments and the structured pastes have been shown to have densely-packed MLV microstructures. At elevated temperatures (e.g. 60 °C), structuring agents are required in order for high-active LAS to form the densely-packed MLVs with shear. Without the structuring agents, a largely planar lamellar microstructure persists and the paste remains softer and ‘unstructured’.

This chapter presents results from experiments in which a variety of salts were sheared with high-active LAS at elevated processing temperatures and found to produce pastes with microstructures of densely-packed MLVs. From these results a better understanding of the mechanisms that are involved in the formation of shear-induced MLVs in high-active LAS will be gained. The results section in this chapter will be divided into three main parts. Firstly, the results from shearing various salts with high-active LAS at 60 °C will be compared. The focus will then be on sodium chloride as a structuring agent and the effect of processing temperature will be considered. Following this, results will be presented for experiments using varying amounts of salt.
5.1 Experimental Description

A brief description of the materials and methods used for the experiments in this section is given below. Further details of the MPR, X-ray unit, and cryo-SEM techniques can be found in Chapter 3.

5.1.1 Materials and Methods

High-active LAS and various salts were used for the experiments that are discussed in this chapter. As in the previous chapter, the MPR was used with the same standard processing conditions (Section 3.2.2.3) to apply shear to the samples. The results that are included in this chapter are for salts that were able to induce tightly-packed MLVs in high-active LAS with shear at 60 °C: ammonium chloride, potassium chloride, sodium chloride, sodium citrate dihydrate, sodium disilicate, sodium nitrate, sodium phosphate dodecahydrate, sodium phosphate monohydrate, tetramethyl-ammonium chloride and tetramethyl-ammonium nitrate. Rheological and X-ray scattering data were obtained from the MPR with attached X-ray unit and cryo-SEM observations were also made of the resultant extrudate.

In the first part of the results section, samples of high-active LAS sheared at 60 °C with various MLV-inducing salts are compared. The amount of salt used with 20 g of high-active LAS for each of the reported experiments was calculated on the basis of adding 0.034 mol of a singly-charged ion (e.g. K⁺, Na⁺, NH₄⁺, NO₃⁻) present in the salt to the paste. This corresponds to 10 wt. % of sodium chloride added to high-active LAS and was chosen to be equivalent to the 10 wt. % of sodium disilicate added to high-active LAS in the experiments described in Chapter 4. The appropriate amounts (in grammes) of the salts used are listed in Table 3.2.

The remainder of the results section will examine the effect of sodium chloride when high-active LAS is sheared. Firstly using a concentration of 0.034 mol sodium chloride to 20 g high-active LAS (i.e. 10 wt. % NaCl), the effect of process temperature (i.e. 40, 60 and 75 °C) is considered. Following that, a comparison with results from shearing 0.0034 mol sodium chloride with 20 g high-active LAS (i.e. 1 wt. % NaCl) at 60 °C is made.
5.2 Results and Discussion

5.2.1 Salts Inducing MLVs at 60 °C

In Chapter 4, the behaviour of high-active LAS with shear at 60 °C was examined both with and without sodium disilicate. It was found that at the temperature and shearing conditions used, sodium disilicate was necessary to induce MLV microstructures from the largely planar lamellar microstructure that would otherwise exist in the high-active LAS. The focus of the present section is to present evidence for MLVs formed from shearing high-active LAS with the salts investigated at 60 °C and to compare the resultant processed pastes. Details of the salt concentrations used for these experiments are found in Section 5.1.1.

5.2.1.1 Rheological Results from the MPR

In the graphs shown in Figure 5.1, typical rheological results obtained from experiments where various salts have been sheared with high-active LAS at 60 °C are displayed. The graphs are of the pseudo-steady state pressure, \( \Delta P_p \), plotted against processing time; results from shearing with the different salts are grouped according to whether the processed pastes exhibit (a) ‘high’ values of \( \Delta P_p \) (above ca. 50 bar), or (b) ‘low’ values of \( \Delta P_p \) (below ca. 40 bar). In order to gauge the level of uncertainty in the rheological measurements, 90 % confidence intervals (calculated from the Student’s \( t \)-distribution) are shown at 60 minutes of shear.

From Figure 5.1 (a), the salts that were investigated and found to result in ‘high’ values of \( \Delta P_p \) (corresponding to processed pastes that appear qualitatively stiff and ‘structured’) were sodium chloride, sodium citrate dihydrate, sodium disilicate, sodium phosphate dodecahydrate and sodium phosphate monohydrate. The general behaviour of high-active LAS processed with these salts is characterised by an initial period of strongly rheopectic behaviour, which is followed by a more weakly rheopectic period leading to rheological steady state. However, high-active LAS processed with sodium phosphate dodecahydrate does not behave in this manner with shear; instead, erratic behaviour is observed. The high proportion of water molecules within the sodium phosphate dodecahydrate salt is likely to contribute to the unexpected rheological behaviour observed, as
paste processed with sodium phosphate monohydrate exhibits the usual rheopectic behaviour.

The salts found to result in ‘low’ values of $\Delta P_p$ when sheared with high-active LAS at 60 °C were ammonium chloride, sodium nitrate, tetramethyl-ammonium chloride, tetramethyl-ammonium nitrate and potassium chloride (Figure 5.1 (b)). Qualitatively these processed pastes appeared softer and not as stiff or ‘structured’ as the pastes exhibiting ‘high’ values of $\Delta P_p$ shown in Figure 5.1 (a).

It is evident from the graphs that there is a significant difference in $\Delta P_p$ values between the two groups of pastes. The characteristic rheological behaviour exhibited by samples featuring in Figure 5.1 (b) begins with a weakly rheopectic initial period followed by rheological steady state.

The rheopectic behaviour observed for the pastes sheared with the various salts in Figure 5.1 appears to be a general characteristic of systems where shear-induced MLVs are formed (McKeown, 2001; Bergenholtz and Wagner, 1996; Läuger et al., 1996). Rheological measurements though useful, are not adequate when used alone for confirming the presence of MLVs and further results from complementary characterisation techniques are needed in order to confirm the presence of MLVs in the pastes that have been discussed in this section.

### 5.2.1.2 X-ray Diffraction Results

X-ray diffraction results were obtained for samples sheared with various salts in the MPR. In this section, data regarding the orientation of microstructures present in the processed pastes will be presented and the characteristic bilayer spacing of samples sheared with different salts will be compared.

#### Orientation of Microstructure

In Figure 5.2, graphs of X-ray intensity versus azimuthal angle, $\chi$, are presented for high-active LAS sheared with various salts at 60 °C in the MPR using standard processing conditions. These orientation profiles are shown after 20 minutes of shear for the majority of paste samples and after 30 minutes for pastes sheared with sodium disilicate and potassium chloride. This discrepancy in time was due to data collected at different times during experiments. Since there were no changes observed in the orientation profiles for samples sheared
from 20 to 50 minutes and in samples sheared from 30 to 50 minutes, the comparison of orientation profiles at 20 and 30 minutes was deemed acceptable. The results from salts found to produce pastes with ‘high’ and ‘low’ $\Delta P_p$ values are shown in Figures 5.2 (a) and (b) respectively. The data series are plotted as continuous lines and shifted along the y-axis for clarity.

The orientation profiles shown in Figure 5.2 have a fairly even distribution of X-ray intensity for all angles of $\chi$; this is more apparent when they are compared to the orientation profiles in Figure 4.2, where sharp peaks in intensity corresponding to aligned planar lamellae are observed. The absence of sharp peaks in Figure 5.2 for both the pastes with ‘high’ and ‘low’ $\Delta P_p$ values indicate that these pastes do not possess aligned microstructures and that densely-packed MLVs, seen in Chapter 4 for high-active LAS processed with sodium disilicate, are likely to be present. Further evidence for MLVs in these processed pastes will be given in Section 5.2.1.3, where cryo-SEM results are discussed.

◊ **Length of the Characteristic Repeating Microstructure Unit (d-spacing)**

A graph of the d-spacing results obtained at steady state (where the d-spacing remains constant with further shear) for the processed pastes exhibiting both ‘high’ and ‘low’ $\Delta P_p$ values is shown in Figure 5.3. Error bars indicating the 90% confidence intervals (calculated from the Student’s $t$-distribution) for pastes sheared with all salts are shown. However, error bars are not shown for paste samples processed with ammonium chloride or potassium chloride, as these results were obtained from single experiments. For comparison, the 90% confidence interval for high-active LAS sheared without added salts at the same processing conditions is represented by a pair of dotted pink lines extending across the graph. From Figure 5.3, apart from a few exceptions, it is evident that processed pastes exhibiting both ‘high’ and ‘low’ $\Delta P_p$ values, do not possess significantly different d-spacing values (or bilayer repeat distances) from high-active LAS sheared without added salts. The pastes with significantly larger d-spacing values were those sheared with sodium phosphate dodecahydrate, tetramethyl-ammonium chloride and tetramethyl-ammonium nitrate. The increase in the bilayer repeat distance for paste processed with sodium phosphate dodecahydrate ($\text{Na}_3\text{O}_4\text{P}\cdot12\text{H}_2\text{O}$) is likely to be due to the addition of a
large number of water molecules associated with the salt. For pastes sheared with tetramethyl-ammonium chloride and tetramethyl-ammonium nitrate, there are no additional water molecules introduced. Instead, the size of the constituent ions appears to be a significant factor in the increased d-spacing values found in samples of high-active LAS sheared with added salts. From calculations estimating the ‘effective size’ of the ionic species used in experiments (Appendix D), the sizes of both the positive and negative species in the system appear important. A summary of the estimated ion sizes introduced with the added salts can be found in Table 5.1. In comparison to the other salts that have been studied, the sizes of both the positive and negative ions introduced with the tetramethyl-ammonium chloride and tetramethyl-ammonium nitrate salts are large. Although the citrate ion is relatively large, as it is not singly-charged, fewer moles were added during experiments in proportion to the constant number of sodium ions that were used for experiments. This may explain why the X-ray d-spacing obtained from high-active LAS sheared with sodium citrate is not significantly different from the d-spacing obtained from high-active LAS sheared without added salts.

5.2.1.3 Cryo-SEM Results

Cryo-SEM observations were made of high-active LAS samples sheared with the salts investigated in this chapter. As all the samples possessed microstructures of densely-packed MLVs, only images representative of sheared pastes exhibiting ‘high’ and ‘low’ $\Delta P_p$ values due to processing with sodium citrate dihydrate (Figure 5.4 (a)) and ammonium chloride (Figure 5.4 (b)) respectively, are shown. From these cryo-SEM images, it is evident that though both pastes consist of densely-packed MLVs, the MLVs are more monodisperse and smaller in the paste sheared with sodium citrate dihydrate than those present in paste sheared with ammonium chloride.

The results from quantitative size analysis of the MLV populations in various paste samples are summarised in the cumulative frequency distribution curves shown in Figure 5.5 (see Section 3.3.2.3 for details of the size analysis method). For clarity, data points are graphed as continuous lines; thick and thin lines are used to represent pastes that exhibit ‘high’ and ‘low’ $\Delta P_p$ values, respectively. In
general, pastes that exhibit ‘high’ $\Delta P_p$ values have steeper cumulative frequency distribution curves than pastes with ‘low’ $\Delta P_p$ values, meaning that these pastes have MLV populations with a narrower size range. In addition, pastes with ‘high’ $\Delta P_p$ values appear to consist of smaller MLVs overall: in such samples ~100% of the MLVs present are smaller than 0.6 µm. However, in pastes exhibiting ‘low’ $\Delta P_p$ values, MLVs larger than 0.6 µm are present.

5.2.1.4 Discussion

From the results that have been presented, it is evident that in addition to sodium disilicate (the structuring agent used for industrial processing), a variety of salts can be used to induce MLVs when sheared with high-active LAS at 60 °C. Some of the salts produce stiff pastes with ‘high’ $\Delta P_p$ values, much like the ‘structured’ paste produced with sodium disilicate. Other salts produce soft pastes with ‘low’ $\Delta P_p$ values. Surprisingly, these pastes also possess MLV-rich microstructures, despite having $\Delta P_p$ values of a similar magnitude when sheared, as pastes with aligned planar lamellae (see Chapter 4).

In comparison to the planar bilayer repeat distance present in high-active LAS sheared at 60 °C without added salts, the bilayer repeat distances present in the pastes sheared with MLV-inducing salts are not affected consistently, implying that MLV formation is not dependent on the bilayer repeat distance. The results also indicate that the paste stiffness (i.e. the magnitude of $\Delta P_p$ values) is not related to the d-spacing values but rather to the size and size range of MLVs within the paste microstructure.

5.2.2 Sodium Chloride Sheared with High-Active LAS: Effect of Temperature

The previous section outlined the response of high-active LAS when sheared at 60 °C with various MLV-inducing salts. In the current section the response of high-active LAS when sheared with sodium chloride (10 wt. %) will be examined at various processing temperatures. This will provide results that can be compared to those obtained from processing with sodium disilicate in Chapter 4.
5.2.2.1  **Rheological Results from the MPR**

Typical rheological results obtained from MPR experiments of high-active LAS sheared with sodium chloride at various processing temperatures (40, 60 and 75 °C) are shown in Figure 5.6. The graph that is shown is of the pseudo-steady state pressure, $\Delta P_p$, plotted against processing time with 90 % confidence intervals (calculated from the Student’s $t$-distribution) shown at 60 minutes of shear. For pastes processed at all the investigated temperatures, an initial period of strongly rheopectic behaviour is exhibited, followed by rheological steady state or further rheopectic behaviour. After 60 minutes of shear, there is no significant difference in the magnitude of $\Delta P_p$ values between pastes processed with sodium chloride at the different temperatures. In comparison to high-active LAS sheared with sodium disilicate (Figure 4.6), samples of high-active LAS sheared with sodium chloride exhibit similar $\Delta P_p$ values (ca. 85 bar) after 60 minutes of shear: the 90 % confidence intervals overlap. Qualitative observations indicate that these ‘high’ $\Delta P_p$ values correspond to firm, ‘structured’ pastes.

5.2.2.2  **X-ray Diffraction Results**

◊  **Orientation of Microstructure**

In Figure 5.7, graphs of X-ray intensity versus azimuthal angle, $\chi$, are shown for high-active LAS sheared with sodium chloride at (a) 40 °C, (b) 60 °C and (c) 75 °C. The data series are plotted as continuous lines for clarity and shifted along the y-axis. From the samples compressed to 4 bar (represented by the yellow lines) some variation in the orientation profiles can be observed, similar to that seen for compressed samples with sodium disilicate (Figure 4.8). As discussed previously, the variation in the profiles is likely to be due to inconsistencies in the pre-mixing and sample loading processes as well as the alignment of the X-ray beam relative to the capillary.

From Figure 5.7, it is clear that there is some change in the microstructure of the paste samples when shearing occurs, as the red lines (for X-ray measurements initiated immediately when shearing first commences) are different from the yellow lines corresponding to compressed static samples. As the X-ray
measurements require 300 s of collection time, it is evident that much of the change in microstructure occurs before the sample has been sheared for 5 minutes. It is interesting that after 20 and 50 minutes of shear, samples processed at 60 and 75 °C produce orientation profiles that have even distributions of X-ray intensity while the orientation profile obtained at 40 °C though fairly ‘flat’ exhibits slight peaks in X-ray intensity at χ = 90° and 270°. These features have also been observed for pastes sheared with sodium disilicate at the same temperatures (Chapter 4) and are likely to be the results of a biphasic microstructure, which will be discussed in Chapter 7.

◊ Length of the Characteristic Repeating Microstructure Unit (d-spacing)

The d-spacing values obtained from paste processed with sodium chloride at various temperatures are shown in Figure 5.8. The 90 % confidence intervals are marked and in addition the 90 % confidence interval for d-spacing results obtained from high-active LAS sheared without any added salts is shown. It is evident that the bilayer repeat distances present in high-active LAS samples sheared with sodium chloride are not significantly different from when sodium chloride is not used, and also that the process temperature has no effect.

5.2.2.3 Cryo-SEM Results

In Figure 5.9, cryo-SEM images are shown of high-active LAS sheared for 60 minutes with sodium chloride at (a) 40 °C, (b) 60 °C and (c) 75 °C. It is evident that these pastes possess tightly-packed MLV microstructures of similar size that are comparable to the resultant microstructures obtained from shearing high-active LAS with sodium disilicate (Figure 4.9).

5.2.2.4 Discussion

It is clear from the evidence that has been presented that sodium chloride has a similar effect to sodium disilicate when sheared with LAS at similar processing conditions: at elevated temperatures tightly-packed MLV microstructures are formed corresponding to ‘structured’ pastes exhibiting ‘high’ ΔPp values. The use of sodium chloride as an alternative industrial structuring agent to sodium disilicate is economically attractive; initial price estimates obtained from
suppliers in the United Kingdom are £30 per 100 kg of sodium chloride and £110 per kg of sodium disilicate. However in order to assess the suitability of sodium chloride as a structuring agent for industrial-scale processes, additional factors such as the corrosive nature of the salt on the processing equipment and the effect of changing the detergent formulation on its performance must also be considered.

5.2.3 Sodium Chloride Sheared with High-Active LAS: Effect of Varying the Amount of Structuring Agent

In the results that have been presented so far, the effect of salt concentration on the shear-induced behaviour of high-active LAS has not been examined. This is clearly an important parameter that deserves investigation. Due to time constraints, it was not possible to carry out an in-depth examination of salt concentration for all the salts used in this work. As a preliminary study, high-active LAS was sheared at 60 °C with 1 wt. % and 10 wt. % of sodium chloride (i.e. 0.0034 mol NaCl and 0.034 mol NaCl added to 20 g of high-active LAS, respectively); in the current section, results from these experiments will be compared.

5.2.3.1 Rheological Results from the MPR

The typical rheological response of high-active LAS sheared at 60 °C in the MPR with 1 wt. % and 10 wt. % sodium chloride is shown in Figure 5.10, where the pseudo-steady state pressure difference, \( \Delta P_p \), is plotted against processing time and 90 % confidence intervals are marked at the end of processing. Rheoplectic behaviour, as discussed previously in Section 2.2.1, is displayed for the sample sheared with 10 wt. % sodium chloride. Interestingly, samples sheared with 1 wt. % sodium chloride exhibit a ‘flat’ period of typically 10 minutes where values of \( \Delta P_p \) are steady with shear, before strongly rheoplectic behaviour is observed. After 60 minutes of shear, despite the differences in rheoplectic behaviour that are observed, both samples exhibit similar ‘high’ \( \Delta P_p \) values (ca. 95 bar) and appear qualitatively ‘structured’ and firm.
5.2.3.2 X-ray Diffraction Results

◊ Orientation of Microstructure
In Figure 5.11, orientation profiles are shown for high-active LAS sheared with (a) 1 wt.% and (b) 10 wt.% sodium chloride at 60 °C. From these graphs, a change in microstructure occurring with shear can be observed. The orientation profiles obtained from compressed static samples (yellow lines) exhibit sharper peaks of X-ray intensity at \( \chi = 90^\circ \) and \( 270^\circ \) than when samples are sheared (red and blue lines); the flatter orientation profiles suggest that MLV microstructures are formed. As previously discussed, the slight peaks of X-ray intensity still present in the orientation profile taken after 50 minutes of shearing with 1 wt.% sodium chloride is indicative of a biphasic microstructure where planar lamellae coexist with MLVs.

◊ Length of the Characteristic Repeating Microstructure Unit (d-spacing)
The X-ray d-spacing values for samples of high-active LAS sheared at 60 °C in the MPR with 1 wt.% and 10 wt.% sodium chloride are shown in Figure 5.12 with the results for high-active LAS sheared without added salts; the 90 % confidence intervals are marked. Although there appears to be a significant difference between results for samples of high-active LAS processed without sodium chloride and with 1 wt.% sodium chloride; there is no significant difference between samples of high-active LAS processed without sodium chloride and with 10 wt.% sodium chloride. Given that samples sheared with 1 wt.% and 10 wt.% sodium chloride do not have significantly different d-spacings, it is not clear what the conclusions that can be drawn from these results might be. It is likely that using a greater level of confidence to calculate the confidence intervals will result in no significant difference between the results obtained for the three conditions.

5.2.3.3 Cryo-SEM Results
The cryo-SEM images of high-active LAS sheared at 60 °C in the MPR after 60 minutes with 1 wt.% and 10 wt.% sodium chloride are shown in Figures 5.13 (a) and (b) respectively. Both images show the tightly-packed MLV microstructures expected from the rheological data and orientation profiles
presented earlier, however it is apparent that there are not as many ‘small’ MLVs (less than ca. 200 nm) in Figure 5.13 (a). It is possible that this is a result of the delayed rheopectic response observed for samples sheared with 1 wt.% sodium chloride (Figure 5.10) as this implies that MLVs are effectively formed later during the shearing process and are therefore less subject to further shear-induced microstructural modifications. Further discussions regarding the effect of the duration of shear on MLVs will be presented in Chapter 7.

5.2.3.4 Discussion

The results that were obtained from shearing high-active LAS at 60 °C with 1 wt.% sodium chloride show that this reduced amount of sodium chloride is effective in inducing MLVs within the microstructure of high-active LAS. Indeed if the magnitude of ∆Pp values that arise as a result of shear are used as a measure of the firmness or ‘structured’ nature of the paste, then over time the same level of firmness can be achieved using either 1 wt.% or 10 wt.% sodium chloride. Thus the duration of the shearing process is important to consider when assessing the optimum salt concentration to use for structuring high-active LAS. It would be interesting to extend this preliminary study to investigate the effect of even lower concentrations of sodium chloride and whether a minimum salt concentration for MLV formation exists or if delayed rheopectic behaviour is also observed at these lower concentrations.

5.3 Chapter Summary

In this chapter, a variety of salts were sheared with high-active LAS at elevated processing temperatures and found to produce pastes with microstructures of densely-packed MLVs. From these results, the pastes could be grouped into firm pastes exhibiting ‘high’ ∆Pp values and soft pastes with ‘low’ ∆Pp values. The size and size range of MLVs within the paste microstructure were found to be related to the magnitude of ∆Pp values when sheared, however these were independent of the repeat distance of the bilayers within the MLVs. The large repeat distances of some samples could be attributed to the addition of salts with large numbers of associated water molecules or salts consisting of bulky anions and cations. Sodium chloride was found to be as effective a structuring agent as
sodium disilicate at elevated processing temperatures and was highlighted as a possible alternative to sodium disilicate as an industrial structuring agent. A comparison of 1 wt. % and 10 wt. % sodium chloride showed that MLV microstructures could be induced at 60 °C and that a comparable level of ‘structuring’ or paste firmness could be achieved over time.
Table 5.1. Summary of added salts and the effective sizes of ions that are introduced during the shearing experiments with high-active LAS. The X-ray d-spacing results from pastes sheared with the added salts are given in comparison to the d-spacing obtained from LAS paste without added salts. The ion sizes that are shown are for single ions and do not take into account the molar ratio within the salt. The presence of water molecules is indicated in proportion to a constituent ion within the salt of interest. The calculations used to obtain the effective size of the ions is found in Appendix D. The effective size of water was estimated as 1.5 Å.

<table>
<thead>
<tr>
<th>Salt sheared with high-active LAS</th>
<th>Effective size of positive ion (Å)</th>
<th>Effective size of negative ion (Å)</th>
<th>Water molecules associated with the salt</th>
<th>X-ray d-spacing in relation to high-active LAS sheared without added salts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium chloride</td>
<td>2.2</td>
<td>3.6</td>
<td>n/a</td>
<td>No difference</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>2.7</td>
<td>3.6</td>
<td>n/a</td>
<td>Smaller</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>1.9</td>
<td>3.6</td>
<td>n/a</td>
<td>No difference</td>
</tr>
<tr>
<td>Sodium citrate (dihydrate)</td>
<td>1.9</td>
<td>7.1</td>
<td>2mol H₂O:1mol Na⁺</td>
<td>No difference</td>
</tr>
<tr>
<td>Sodium disilicate</td>
<td>1.9</td>
<td>5.5</td>
<td>n/a</td>
<td>Smaller</td>
</tr>
<tr>
<td>Sodium nitrate</td>
<td>1.9</td>
<td>3.4</td>
<td>n/a</td>
<td>No difference</td>
</tr>
<tr>
<td>Sodium phosphate monobasic monohydrate</td>
<td>1.9</td>
<td>4.6</td>
<td>1mol H₂O:1mol Na⁺</td>
<td>Smaller</td>
</tr>
<tr>
<td>Sodium phosphate tribasic dodecahydrate</td>
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<td>4.0</td>
<td>4 mol H₂O:1mol Na⁺</td>
<td>Larger</td>
</tr>
<tr>
<td>TMA-chloride</td>
<td>6.6</td>
<td>3.6</td>
<td>n/a</td>
<td>Larger</td>
</tr>
<tr>
<td>TMA- nitrate</td>
<td>6.6</td>
<td>3.4</td>
<td>n/a</td>
<td>Larger</td>
</tr>
</tbody>
</table>
Chapter 5: Further Salts Inducing MLVs with Shear

Figure 5.1. Typical response of high-active LAS sheared with various salts in the MPR using standard processing parameters at 60 ºC; the pseudo-steady state pressure difference is plotted against processing time. The resultant pastes are grouped according to: (a) ‘high’ values of \( \Delta P_p \) or (b) ‘low’ values of \( \Delta P_p \). The proportion of salt to LAS was fixed by having 0.034 mol of K\(^+\), Na\(^+\) or NH\(_4\)\(^+\) within the salt to 20 g of high-active LAS. The 90 % confidence intervals for \( \Delta P_p \) (calculated using the Student’s \( t \)-distribution) are shown at 60 minutes of processing time.
Figure 5.2. X-ray intensity versus azimuthal angle, $\chi$, for high-active LAS sheared at 60 °C with various salts in the MPR using standard processing parameters. The salts are grouped according to whether the resultant paste exhibits (a) ‘high’ values of $\Delta P_p$ or (b) ‘low’ values of $\Delta P_p$. The proportion of salt to LAS was fixed by having 0.034 mol of K$^+$, Na$^+$ or NH$_4^+$ within the salt to 20 g of high-active LAS. Data are shown after 20 minutes of shear (except for sodium disilicate and potassium chloride, where results are shown after 30 minutes of shear). The data series are plotted as continuous lines and shifted along the y-axis for clarity.
Figure 5.3. Steady state X-ray d-spacing values obtained from high-active LAS paste samples during shear in the MPR (standard processing conditions were used). Results are shown for LAS sheared with various salts at 60 °C. The proportion of salt to LAS was fixed by having 0.034 mol of K⁺, Na⁺ or NH₄⁺ within the salt to 20 g of high-active LAS. The 90% confidence intervals for the X-ray d-spacing values (calculated using the Student’s t-distribution) are shown.
Figure 5.4. Cryo-SEM images of high-active LAS after shearing for 60 minutes at 60 °C in the MPR using standard processing conditions with (a) sodium citrate dihydrate (‘high’ $\Delta P_p$ values) and (b) ammonium chloride (‘low’ $\Delta P_p$ values). The proportion of salt to LAS was fixed by having 0.034 mol of $\text{Na}^+$ or $\text{NH}_4^+$ within the salt to 20 g of high-active LAS.
Chapter 5: Further Salts Inducing MLVs with Shear

Figure 5.5. Cumulative frequency distribution of MLV sizes typically present in samples of high-active LAS paste sheared at 60 °C with various salts for 60 minutes in the MPR (using standard processing conditions). The proportion of salt to LAS was fixed by having 0.034 mol of K⁺, Na⁺ or NH₄⁺ within the salt to 20 g of high-active LAS. For clarity, data points are graphed as continuous lines. Samples that exhibited ‘high’ ∆Pₚ are represented by thick lines and samples that exhibited ‘low’ ∆Pₚ are represented by thin lines.
Figure 5.6. Typical response of high-active LAS sheared with sodium chloride in the MPR using standard processing parameters at various temperatures; the pseudo-steady state pressure difference is plotted against processing time. 10 wt. % of sodium chloride (i.e. 0.034 mol of Na+ within the salt) was added to 20 g of high-active LAS for all the experiments. The 90 % confidence intervals for $\Delta P_p$ (calculated using the Student’s $t$-distribution) are shown at 60 minutes of processing time.
Figure 5.7. X-ray intensity versus azimuthal angle, $\chi$, for high-active LAS sheared in the MPR with sodium chloride using standard processing parameters. Typical results are shown for processing at (a) 40 °C, (b) 60 °C and (c) 70 °C. 10 wt. % of sodium chloride (i.e. 0.034 mol of Na$^+$ within the salt) was added to 20 g of high-active LAS for all the experiments. The data series are plotted as continuous lines and shifted along the y-axis for clarity.
Figure 5.8. Steady-state X-ray d-spacing values obtained from high-active LAS paste samples sheared with sodium chloride in the MPR using standard processing parameters at various temperatures. 10 wt. % of sodium chloride (i.e. 0.034 mol of Na⁺ within the salt) was added to 20 g of high-active LAS for all the experiments. The 90 % confidence intervals for the X-ray d-spacing values (calculated using the Student’s $t$-distribution) are shown.
Figure 5.9. Cryo-SEM images of high-active LAS sheared with sodium chloride after 60 minutes in the MPR using standard processing conditions at (a) 40 °C, (b) 60 °C and (c) 75 °C. 10 wt. % of sodium chloride (i.e. 0.034 mol of Na⁺ within the salt) was added to 20 g of high-active LAS for all the experiments.
Figure 5.10. Typical response of high-active LAS sheared with different amounts of sodium chloride in the MPR using standard processing parameters at 60 °C; the pseudo-steady state pressure difference is plotted against processing time. The amount (in moles) of sodium chloride used for each experiment is in proportion to 20 g of high-active LAS. The 90 % confidence intervals for $\Delta P_p$ (calculated using the Student’s $t$-distribution) are shown at 60 minutes of processing time.
Figure 5.11. X-ray intensity versus azimuthal angle, $\chi$, for high-active LAS sheared in the MPR with different concentrations of sodium chloride at 60 °C using standard processing parameters. In the experiments, added to 20 g high-active LAS are: (a) 0.0034 mol sodium chloride and (b) 0.034 mol sodium chloride. The data series are plotted as continuous lines and shifted along the y-axis for clarity.
Figure 5.12. Steady-state X-ray d-spacing values obtained from high-active LAS paste samples sheared with different concentrations of sodium chloride at 60 °C in the MPR using standard processing parameters. The 90 % confidence intervals for the X-ray d-spacing values (calculated using the Student’s $t$-distribution) are shown.
Figure 5.13. Cryo-SEM images of high-active LAS sheared with different concentrations of sodium chloride after 60 minutes in the MPR at 60 °C using standard processing conditions. In the experiments, added to 20 g high-active LAS are: (a) 0.0034 mol sodium chloride and (b) 0.034 mol sodium chloride.
Chapter 6

Effect of Time on MLV Formation and Stability

From the evidence presented in previous chapters, we have seen that with shear, high-active LAS can form various microstructures, particularly MLVs, depending on the salt added and processing temperature. In Chapter 4, a link was made between MLVs and industrially ‘structured’ LAS paste, demonstrating that studies on MLV formation are not only interesting from a scientific perspective, but also from an industrial viewpoint. In Chapter 5, various salts were then seen to induce the formation of MLVs in high-active LAS when sheared at 60 °C in the MPR. These previous chapters have used X-ray diffraction data and cryo-SEM images to study the microstructure of processed LAS paste samples. The X-ray diffraction data have allowed the bilayer repeat distance and the degree of orientation within the sample microstructure to be monitored throughout the shearing process, while the size of the MLVs determined from cryo-SEM images have been obtained at the end of the shearing process.

During the MLV-inducing experiments that have been discussed in Chapters 4 and 5, paste samples were sheared for a fixed period of 60 minutes, and MLV sizes were then compared. From these experiments, the effect of the duration of shear or processing time on the MLV sizes within the sample microstructure was not considered. The connection between paste firmness and MLV size has been made in Chapter 5; coupled with the rheopectic behaviour observed from LAS pastes with MLV-rich microstructures, it is therefore possible that there is some dependency of MLV size on the duration of applied shear. This will form the basis for the first part of the present chapter.

The results presented so far in this thesis have concentrated on the microstructures that are formed in high-active LAS with shear and that are present during the shearing process. However when shear is no longer applied to
the system, it is possible that the stability of the shear-induced microstructures is affected; this has potential implications for processes using materials consisting of such shear-induced microstructures. The second part of this chapter will thus examine the stability of MLVs over time by comparing the effect of added salts and processing temperature during the shearing process on the stability of the resultant MLV microstructures.

6.1 Experimental Description

The materials and methods used for the experiments in this section have been previously described in Chapter 3. High-active LAS paste samples were sheared in the MPR using standard processing parameters with added salts and process temperatures as required.

For the results in Section 6.2.1, where the development of MLV-microstructures with the duration of applied shear is examined, experiments were conducted with high-active LAS paste at 25 ºC with 10 wt. % sodium disilicate. Samples were sheared for 7, 60 and 225 minutes; after the shearing process cryo-SEM images were obtained.

Section 6.2.2 examines the stability of MLVs over time. Experiments were conducted to investigate the effect of added salts and processing temperature on the stability of the resultant MLVs formed. For all these experiments, samples were sheared for 60 minutes. The experiments investigating the effect of added salts were conducted using high-active LAS (a) without added salts at 25 ºC, (b) with 10 wt. % sodium chloride at 60 ºC and (c) with 10 wt. % sodium disilicate at 60 ºC. The remaining experiments used high-active LAS with 10 wt. % sodium disilicate at various processing temperatures: 25, 40 and 60 ºC. After shearing, samples were stored in sealed vials at ca. 18 ºC, and cryo-SEM observations were made at intervals over a month.
6.2 Results and Discussion

As discussed, the results and discussion section has been divided into two main subsections to investigate: (1) the development of MLVs with shear over time and (2) MLV stability over time.

6.2.1 Development of MLVs with Shear Over Time

The results shown in this section are from experiments conducted in the MPR using high-active LAS sheared with 10 wt. % sodium disilicate at 25 °C for varying periods of shear.

6.2.1.1 Rheological Results from the MPR

The typical rheological response of a high-active LAS sample sheared with 10 wt. % sodium disilicate in the MPR at 25 °C is shown in Figure 6.1 for a shearing period of 225 minutes; the pseudo-steady state pressure difference, \( \Delta P_p \), is plotted against shearing time. Dotted lines are used to highlight 7, 60 and 225 minutes of shear, as the corresponding cryo-SEM images for pastes processed for the appropriate shear duration are shown in Figure 6.2 and will be discussed in Section 6.2.1.2. As the sample is sheared, strongly rheopectic behaviour is initially observed, eventually resulting in rheological steady state. The large magnitude of \( \Delta P_p \) values at steady state (ca. 120 bar) coupled with the rheopectic response during shear are similarly seen for a different sample processed under the same conditions (Figure 4.6) and are typical for ‘structured’ LAS paste possessing MLV-rich microstructures.

6.2.1.2 Cryo-SEM Results

◊ MLV Size and Morphology

In Figure 6.2, cryo-SEM images of high-active LAS processed in the MPR at 25 °C with 10 wt. % sodium disilicate are shown; the samples were sheared for (a) 7 minutes, (b) 60 minutes and (c) 225 minutes. The images obtained from the processed samples have a common feature: densely-packed MLVs. There are however, some notable differences between the images depending on the duration of shear that the pastes were subjected to.
After 7 minutes of shear (Figure 6.2 (a)), the size distribution of MLVs (from ca. 10 nm to ca. 50 nm) is wide in comparison to the microstructure obtained after shearing for 225 minutes (Figure 6.2 (c)). Another feature of the microstructure formed after 7 minutes of shear is the typically ellipsoidal rather than spherical shape of the MLVs, where the MLVs appear to be ‘stretched’ in a direction tangential to the circumference of the extrudate cross-section. In comparison, the MLVs formed after 60 minutes of shear (Figure 6.2 (b)) appear to be more spherical in shape although the MLV size distribution is still fairly wide. The densely-packed MLV microstructure produced after 225 minutes of shear (Figure 6.2 (c)) has a much narrower size distribution than those shown in Figures 6.2 (a) and (b) with spherical MLVs present.

◊ Biphasic Planar/MLV Microstructure

Cryo-SEM images of high-active LAS sheared for 7 minutes with 10 wt. % sodium disilicate at 25 °C are shown in Figure 6.3; images are shown at different magnifications. In Figure 6.3 (a), a tightly-packed MLV microstructure is seen similar to that shown in Figure 6.2 (a); also present are planar lamellar fragments that are aligned in the same direction as the MLVs are ‘stretched’ (i.e. with the bilayer normal, \( n \), perpendicular to the tangent of the extrudate circumference). The lower magnification images (Figures 6.2 (b) and (c)) demonstrate more clearly the alignment of planar lamellae and the MLVs that are packed between them. Although further cryo-SEM images are not shown, shearing beyond 7 minutes results in a reduction of the size and number of planar lamellar fragments in the paste microstructure in addition to reducing the average size of MLVs that are also present.

6.2.1.3 Discussion

From the results that have been presented, it is evident that the formation of MLVs in high-active LAS is a time dependent process. The formation of MLVs from planar lamellae can be related to the strongly rheopectic behaviour displayed typically within 20 minutes of shear. This has already been discussed in previous chapters where various MLV-rich samples have had biphasic microstructures (of MLVs and planar lamellae) detected by X-ray diffraction measurements (Figure 4.3, Figures 4.8 (a), (b) and Figure 5.7 (a)). It is
interesting that with shear, the planar lamellae exist in an ordered and well-aligned state even when MLVs form. The persisting orientation detected in the X-ray measurements may also be the result of MLVs being stretched parallel to the direction of flow (Figure 6.2 (a)).

From the evidence presented in Chapter 5, firm pastes with high $\Delta P_p$ values have been associated with microstructures consisting of narrow MLV size distributions and MLVs that are smaller than those present in softer pastes. The results in the present chapter indicate that over time, the effect of shear on the MLV microstructure is to break down large MLVs to form smaller ones; this reduces the MLV size distribution and thus rheopectic behaviour is expected. After the initial period of strongly rheopectic behaviour typically exhibited by pastes with densely-packed MLVs, the rheological response becomes less dependent on time and weakly rheopectic or steady state behaviour is often observed. As the reduction of MLV size occurs over this period, this type of structural transformation does not appear to contribute as significantly to the observed rheopectic behaviour as the transformation from planar lamellae to MLVs.

The time-dependent nature of MLV formation in high-active LAS during the paste-structuring process means that it is likely that both the shear rate and duration of shear contribute to the level of paste structuring or paste firmness that is achieved. The reader is referred to Appendix E for a comparison of the apparent wall shear rates and residence times used in industry with the experimental parameters used in the MPR.

### 6.2.2 MLV Stability Over Time

In this section, experiments were conducted to investigate the effect of added salts and processing temperature on the stability of the resultant MLVs formed. All paste samples were sheared for 60 minutes in the MPR using standard processing parameters and then stored after processing in sealed vials at ca. 18°C for cryo-SEM observations.
6.2.2.1 Effect of Added Salts

The results in this section are from samples of high-active LAS sheared for 60 minutes (a) without added salts at 25 ºC, (b) with 10 wt. % sodium chloride at 60 ºC and (c) with 10 wt. % sodium disilicate at 60 ºC; pastes that form densely-packed MLVs when sheared. In Figure 6.4 cryo-SEM images of the processed pastes are shown after the extrudate samples have been sheared and then stored for (i) 3 weeks and (ii) 5 weeks. By examining the microstructure of the processed pastes over time (once shear is removed), the effect of the different chemical environments on the stability of MLVs can be observed.

When the cryo-SEM images of paste samples stored for 3 weeks are compared (Figures 6.4 (a-i), (b-i) and (c-i)) it is evident that during the storage period the paste samples have undergone different degrees of microstructural modification or ‘aging’. In Figure 6.4 (a-i) which shows the cryo-SEM image obtained for high-active LAS sheared at 25 ºC, the microstructure is dominated by the densely-packed MLVs initially present in the processed paste, the image scale however is such that the larger planar lamellar fragments which are also present are emphasised. These planar lamellar fragments are different from those seen in Figure 6.3, as the fragments appear randomly arranged and not aligned in a particular direction, indicating that the formation of these fragments has occurred during storage, after the shearing process. The MLVs thus must be the equilibrium phase during shear but meta-stable in the absence of shear. The cryo-SEM image for high-active LAS sheared with 10 wt. % sodium chloride at 60 ºC (Figure 6.4 (b-i)) also shows the presence of randomly-arranged planar lamellar fragments amongst the dominant MLV microstructures after 3 weeks of storage. In comparison to Figure 6.4 (a-i), it is apparent that these fragments are smaller and more widely distributed throughout the microstructure of the paste. When the cryo-SEM image for high-active LAS sheared at 60 ºC with 10 wt. % sodium disilicate is examined (Figure 6.4 (c-i)), although the image scale is different, there is no evidence of the planar lamellar fragments that are present in the other ‘aged’ samples.

In Figures 6.4 (a-ii), (b-ii) and (c-ii) cryo-SEM images of the paste samples aged for 5 weeks after processing are presented. With the further storage time, more planar lamellae form in the paste sample sheared at 25 ºC (Figure 6.4 (a-ii)).
planar lamellae are arranged in ‘clusters’ throughout the MLV-microstructure of the paste. Within the clusters the planar lamellae appear to be arranged randomly; this is seen more clearly in Figure 6.5 (a) where the lamellar cluster circled in Figure 6.4 (a-ii) is shown at greater magnification. In Figure 6.4 (b-ii), further storage time also appears to promote the formation of more planar lamellae for LAS paste sheared with sodium chloride at 60 °C; the planar fragments are of a similar size to those seen after 3 weeks of storage (Figure 6.4 (b-i)). The planar lamellae that are circled can be seen under greater magnification in Figure 6.5 (b). For the paste sheared at 60 °C with sodium disilicate after 5 weeks of storage (Figure 6.4 (c-ii)), it is evident that the majority of the paste microstructure is still in the form of MLVs. However, there is some evidence of the formation of planar lamellae in the cryo-SEM image; this lamellar cluster is circled and shown in greater detail in Figure 6.5 (c). The other features that can be seen in Figure 6.4 (c-ii) are not significant: the large blemishes in the image are artifacts from the freeze-fracture preparation of the sample for cryo-SEM and the dark patches in the image are due to ‘beam damage’ that can occur during cryo-SEM observations.

A comparison of the higher magnification images in Figures 6.5 (a), (b) and (c) shows that the planar lamellae appear in similar clusters although the size of the clusters differ. In these images, the MLVs co-existing with the lamellar clusters are also more apparent. Pastes that have been stored and found to consist of lamellar clusters seem qualitatively softer and more ‘adhesive’ than when first sheared.

### 6.2.2.2 Effect of Temperature

The remaining experiments investigate the stability of MLVs in high-active LAS sheared with 10 wt. % sodium disilicate at (a) 25 °C, (b) 40 °C and (c) 60 °C. The cryo-SEM images of the processed paste samples stored for durations ranging between 7 to 24 days are shown in Figure 6.6. For the paste processed at 25 °C with sodium disilicate (Figure 6.6 (a)), it is apparent that lamellar clusters have formed over the 7 days of storage and that these lamellar clusters are dispersed throughout the paste (some clusters are circled for clarity). A lamellar cluster from this paste sample after 24 days of storage is shown under greater
magnification in Figure 6.6 (a-i) where the co-existing MLV-microstructure can also be seen more clearly. The sample of paste sheared at 40 °C and stored for 6 days after processing (Figure 6.6 (b)) also shows the presence of lamellar clusters formed throughout the paste microstructure. A comparison of the lamellar clusters formed from pastes processed at 25 °C and 40 °C is difficult as Figures 6.6 (a) and (b) are at different magnifications. From Figure 6.6 (c) it appears that lamellar clusters have not formed from paste sheared with sodium disilicate at 60 °C even after 18 days of storage after shear and that the MLV-microstructure has stayed intact.

6.2.2.3 Discussion

The results from this section have shown that the shear-induced MLV microstructures are meta-stable in the absence of shear; when shear is no longer applied, the MLVs revert back over time to the more stable planar state. Thus, the application of shear to the high-active LAS system must shift the thermodynamic equilibrium. The planar lamellae that form over time are not subjected to shear and therefore do not align in a particular direction. Instead of this, lamellar clusters are formed where the planes are arranged randomly. The existence of clusters of lamellae suggests the occurrence of secondary nucleation.

From the results, the type of salt added during the shearing process (when the MLVs form) has been shown to affect the stability of MLVs when shear is no longer applied. At a processing temperature of 60 °C, high-active LAS sheared with sodium disilicate produces MLVs with greater stability than those that form when processed with sodium chloride, as hardly any lamellar clusters are observed for the paste processed with sodium disilicate. At 60 °C, high-active LAS requires salts to be added during the shearing process in order for MLVs to form, thus a sample of high-active LAS was sheared at 25 °C in order to produce MLVs without the addition of extra salts. Although the lamellar clusters formed from the paste sheared at 25 °C appear larger and different in quality to those found in the paste processed with sodium chloride, it is not evident whether this is due to the added salt alone or if the processing temperature also has an effect.
In Section 6.2.2.2, the processing temperature was seen to have an effect on the stability of the resultant MLVs. For pastes processed with sodium disilicate, at the lower processing temperatures of 25 °C and 40 °C, MLVs were found to form lamellar clusters after a week whereas the MLVs formed at 60 °C did not revert back to the planar lamellar form when stored for a longer period. It is possible that at the higher processing temperature, the sodium disilicate is more soluble and thus more able to dissolve into the high-active LAS paste than at the lower temperatures and that this could have an effect on the stability of the MLVs.

The cryo-SEM images of MLVs formed from high-active LAS sheared alone at 25 °C, at 60 °C with sodium disilicate and at 60 °C with sodium chloride have been shown in Figures 4.5 (a), 4.9 (c) and 5.9 (b) respectively. The images show that the tightly-packed MLV microstructures differ between the processing conditions. These differences can be related to the stability of the MLVs: MLVs that are more ‘perfectly formed’, i.e. uniform and monodisperse, appear more stable. It is possible that the nucleation of planar lamellae occurs at defect sites in the MLV phase (e.g. isolated lamellae, distorted or very large MLVs).

The meta-stable nature of MLVs in the absence of shear has implications for the industrial use of ‘structured’ LAS pastes. The gradual reversion of MLVs to planar lamellae is detected in the concurrent loss of paste firmness, and this loss of firmness over time agrees with industrial experience. This is why ‘structured’ paste is not stored in industry; to retain its firmness it must be used immediately after it is ‘structured’ and cannot be stored. The effect of a structuring agent on the stability of the MLVs in ‘structured’ LAS pastes is also important as it is more desirable to have a stable material in a process than an unstable one. It is evident that a structuring agent such as sodium disilicate is necessary for creating firm ‘structured’ LAS paste. Although high-active LAS can be ‘structured’ and form MLVs at 25 °C without any additives, a more stable paste is produced at 60 °C with sodium disilicate.

6.3 Chapter Summary

In this chapter, we have seen that the formation of MLVs is a time dependent process that is reflected in the rheopectic behaviour observed for MLV-rich paste
samples. From an initial planar lamellar state where the lamellae align with shear, MLVs form between the lamellae and a biphasic microstructure exists. With increased duration of shear more MLVs form and become more spherical and uniform in size. We have also seen that MLVs are meta-stable with shear and that the application of shear shifts the thermodynamic equilibrium in the high-active LAS system. When the MLVs revert back to their planar lamellar state, lamellar clusters form throughout the paste microstructure and the paste becomes correspondingly less firm. The stability of the MLVs appears to be affected by the processing temperature and salts added during the shearing process.
Figure 6.1. Pseudo-steady state pressure difference, $\Delta P_p$, versus shearing time. The typical rheological response is shown for high-active LAS sheared with 10 wt. % sodium disilicate in the MPR at 25 °C. Dotted lines are used to mark out 7, 60 and 225 minutes of shearing time; in Figure 6.2 corresponding cryo-SEM images for pastes sheared for the appropriate times are shown.
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Figure 6.2. Cryo-SEM images of high-active LAS sheared with 10 wt. % sodium disilicate in the MPR at 25°C for: (a) 7 minutes, (b) 60 minutes and (c) 225 minutes. The arrow in (a) is pointing in a direction tangential to the circumference of the extrudate cross-section.
Figure 6.3. Cryo-SEM images of high-active LAS sheared with 10 wt. % sodium disilicate at 25 °C in the MPR for a duration of 7 minutes; (a), (b) and (c) show images taken at decreasing levels of magnification. The white arrow in (c) points from the centre to the edge of the circular extrudate cross-section.
Figure 6.4. Cryo-SEM images of high-active LAS sheared for 60 minutes in the MPR at: (a) 25 °C without added salts, (b) 60 °C with 10 wt. % sodium chloride and (c) 60 °C with 10 wt. % sodium disilicate. After shearing, images were obtained after samples were stored for: (i) 3 weeks and (ii) 5 weeks. Lamellar clusters are circled in white and can be seen in greater detail in Figure 6.5.
Figure 6.5. Cryo-SEM images of high-active LAS stored for 5 weeks after being sheared for 60 minutes in the MPR at: (a) 25 °C without added salts, (b) 60 °C with 10 wt. % sodium chloride and (c) 60 °C with 10 wt. % sodium disilicate. These images show the structures circled in Figures 6.4 (a-ii), (b-ii) and (c-ii) in more detail.
Figure 6.6. Cryo-SEM images of high-active LAS sheared with 10 wt. % sodium disilicate for 60 minutes in the MPR at: (a) 25 °C, (b) 40 °C and (c) 60 °C. After shearing, images were obtained from paste samples that had been stored for: (a) 7 days, (a-i) 24 days, (b) 6 days and (c) 18 days. A few lamellar clusters are circled in (a) and in (a-i) a lamellar cluster from paste stored over a longer period is shown at a greater magnification.
Chapter 7

SALTS INDUCING NON-MLV MICROSTRUCTURES WITH SHEAR

In Chapters 4 and 5, the effect of various salts on the behaviour of high-active LAS with shear was investigated. The results showed that at the industrially relevant processing temperature of 60 °C, microstructures of tightly-packed MLVs were induced in high-active LAS when sheared with each of the salts discussed; without added salts, a largely planar lamellar microstructure remained. MLVs were also the focus of Chapter 6 where the effect of shear duration on the resultant MLV microstructure and the stability of MLVs over time were examined. In this chapter, results are presented from experiments where further salts have been sheared with high-active LAS at 60 °C. Instead of densely-packed MLVs appearing, other microstructures formed. These results allow further aspects relating to the shear-induced behaviour of high-active LAS to be explored.

This chapter consists of three main subsections, corresponding to the particular shear-induced microstructures that form using the various salts sheared with high-active LAS at 60 °C in the MPR. Firstly, results from salts that do not have a significant effect on the behaviour of high-active LAS with shear will be presented. Following this, results will be shown for high-active LAS sheared in the presence of both an MLV-inducing salt as well as a salt with no significant effect on the microstructure of high-active LAS. The final section will examine results obtained from shearing salts with high-active LAS to produce relatively large, worm-like microstructures that have not been previously reported in the literature.
7.1 Experimental Description

In Chapter 3, detailed descriptions of the materials, equipment, experimental protocol and characterisation techniques used for these experiments are given. The materials and methods used to obtain the results that will be presented are briefly described below.

7.1.1 Materials and Methods

High-active LAS and various salts were used for experiments discussed in this chapter. Experiments were conducted with the MPR to apply shear to samples using the process parameters described previously (Section 3.2.2.3).

The salts sheared with high-active LAS in this chapter were sodium sulfate, sodium sulfite, tri-ammonium citrate, sodium hydroxide and mixtures of sodium chloride and sodium sulfate. The proportion of added salt to high-active LAS was fixed by adding 0.034 mol Na\(^+\) or NH\(_4\)\(^+\) to 20 g of high-active LAS. In Table 3.2 the molecular formulae are listed with the appropriate amounts of salts added per experiment (in grammes). When mixtures of salts were added, the proportion of sodium chloride (NaCl) to sodium sulfate (Na\(_2\)SO\(_4\)) within each mixture was determined by using a Na\(^+\) mol-% basis; thus for NaCl(20%):Na\(_2\)SO\(_4\)(80%) and NaCl(80%):Na\(_2\)SO\(_4\)(20%) the percentages refer to the amount of sodium ions contributed by each of the salts. Although the processing temperature during shear was generally kept at 60 °C, experiments using sodium sulfate were also carried out at 25, 40 and 75 °C.

From the experiments, rheological and X-ray scattering data were obtained from the MPR with attached X-ray unit during shear and cryo-SEM images were taken of the stored extrudate.

7.2 Results and Discussion

Results will be presented for the use of the following salts: (1) sodium sulfate and sodium sulfite, (2) mixtures of sodium chloride and sodium sulfate, and (3) tri-ammonium citrate and sodium hydroxide.
7.2.1 Effect of Sodium Sulfate and Sodium Sulfite on High-Active LAS with Shear

In this section the effect of adding sodium sulfate and sodium sulfite to high-active LAS during shear will be examined at elevated processing temperatures (60 °C, 75 °C). Following this, the effect of sodium sulfate when sheared with high-active LAS at the additional processing temperatures of 25 °C and 40 °C will be compared with high-active LAS sheared without added salts at the corresponding temperatures.

7.2.1.1 Rheological Results from the MPR – Sodium Sulfate and Sodium Sulfite Sheared at 60 °C with High-Active LAS

In Figure 7.1, a graph showing rheological results obtained from experiments in the MPR where various salts have been sheared with high-active LAS at 60 °C is presented. The pseudo-steady state pressure, ΔP_p, is plotted against processing time and the 90 % confidence intervals (calculated from the Student’s t-distribution) are shown at 60 minutes of shear. Although the graph shows results for shearing high-active LAS with a number of different salts, the results that are of interest in this section are for sodium sulfate and sodium sulfite – the results relating to the other salts will form the basis of Sections 7.2.2 and 7.2.3.

From Figure 7.1, it is evident that the rheological response of high-active LAS sheared with sodium sulfate at 60 °C is very similar to that observed with sodium sulfite. With the two salts, rheological steady state is achieved immediately as the samples are sheared in the MPR and ΔP_p values of ca. 8 bar are obtained. These results are not significantly different from the rheological response of high-active LAS sheared without added salts at 60 °C and 75 °C (Figure 4.1). It is thus reasonable to expect similar microstructures for the samples sheared with sodium sulfate and sodium sulfite. The microstructure of the sheared samples will be discussed in the following sections.
7.2.1.2 X-ray Diffraction Results – Sodium Sulfate and Sodium Sulfite Sheared at 60 °C with High-Active LAS

◊ Orientation of Microstructure

Typical graphs of X-ray intensity versus azimuthal angle, χ, are presented in Figure 7.2 for high-active LAS sheared with (a) sodium sulfate and (b) sodium sulfite – these were obtained from the X-ray diffraction measurements made during shearing experiments in the MPR at 60 °C using standard processing parameters. Data are shown prior to shear where the sample was compressed to 4 bar, and after 20 and 50 minutes of shear.

From Figure 7.2, both the samples processed with sodium sulfate and sodium sulfite can be seen to comprise of microstructures with aligned planar lamellae, as the orientation profiles exhibit peaks of X-ray intensity at χ = 90° and 270°. The unchanging orientation response shown by the samples during compression and throughout the shearing process implies that the alignment of the planar lamellae is present at the beginning of the experiment and this remains the case throughout the shearing process. This type of response is similar to that observed in the orientation profiles displayed in Figures 4.3 (c) and (d) which correspond to the aligned planar lamellae microstructure of high-active LAS samples when sheared (without added salts) at 60 °C and 75 °C respectively.

◊ Length of the Characteristic Repeating Microstructure Unit (d-spacing)

In Figure 7.3, the d-spacing values obtained at steady state (where the d-spacing remains constant over time at a given shear rate) are shown for high-active LAS sheared at 60 °C in the MPR with sodium sulfate and sodium sulfite. To give an indication of the errors, the 90 % confidence intervals (calculated from the Student’s t-distribution) have been included; results from shearing high-active LAS without added salts at 60 °C are shown for comparison. Although results for samples processed with mixtures of salts have also been plotted in Figure 7.3, these will be discussed later in Section 7.2.2.

It can be seen that the d-spacing values, and hence the bilayer repeat distance, are not significantly different between samples of high-active LAS sheared with sodium sulfate and sodium sulfite. Also, the samples sheared with the salts do
not appear significantly different from high-active LAS sheared without added salts at 60 ºC, although there is greater variation in the d-spacing values.

7.2.1.3 Cryo-SEM Results – Sodium Sulfate and Sodium Sulfite Sheared at Elevated Temperatures with High-Active LAS

Cryo-SEM images for high-active LAS sheared at elevated temperatures with sodium sulfate at 75 ºC and sodium sulfite at 60 ºC are shown in Figures 7.4. (a) and (b) respectively, at decreasing magnification from (i) to (ii). Shearing was conducted in the MPR using standard processing parameters for 60 minutes. Cryo-SEM images were not available for samples sheared with sodium sulfate at 60 ºC. However from the rheological data presented in Figure 7.5 and X-ray data (not included here), the microstructure obtained from samples sheared at 75 ºC is likely to be very similar and is shown instead. The rheological and microstructural behaviour exhibited by high-active LAS sheared with sodium sulfate and sodium sulfite is similar to that of high-active LAS sheared without added salts (Chapter 4); this will be further discussed in the following sections.

From Figure 7.4, the microstructures of the samples sheared at elevated temperatures are very similar. In Figures 7.4 (a-ii) and (b-ii), the tightly-packed MLV microstructures found in firm, ‘structured’ pastes are not observed, instead the images correspond to microstructures comprised largely of planar lamellae, as suggested by the orientation profiles in Figure 7.2. The higher magnification images in Figures 7.4 (a-i) and (b-i) show some evidence of MLV-like microstructures though these do not form a tightly-packed matrix; these structures are similar to those seen in Figures 4.5 (b), (c) and (d) for samples of high-active LAS sheared without added salts at elevated temperatures.

7.2.1.4 Rheological Results from the MPR – Sodium Sulfate Sheared at Various Temperatures with High-Active LAS

As the rheological and microstructural response of high-active LAS sheared with sodium sulfate and sodium sulfite is similar to that of high-active LAS sheared without added salts at elevated temperatures (60 ºC and 75 ºC), it is also reasonable to expect similar behaviour to be observed at other temperatures.
Evidence for this will now be presented by examining the results obtained from shearing high-active LAS with sodium sulfate at 25, 40, 60 and 75 °C.

Figure 7.5 presents a graph of the typical rheological response of high-active LAS sheared with sodium sulfate in the MPR using standard processing parameters at various temperatures. The pseudo-steady state pressure difference, \( \Delta P_p \), is plotted against processing time and the 90% confidence intervals (calculated from the Student’s \( t \)-distribution) are shown at 60 minutes of shear. In comparison to Figure 4.1, where the rheological response for high-active LAS sheared without added salts is plotted, a similar response is indeed observed at the temperatures investigated. The \( \Delta P_p \) values are of the same order of magnitude and rheological steady state is achieved after 60 minutes of shear. As was the case for samples sheared without added salts, samples processed at 60 °C and 75 °C do not exhibit significantly different rheological responses and values of \( \Delta P_p \) are low at ca. 8 bar. At 40 °C significantly larger values of \( \Delta P_p \) at ca. 30 bar are observed while at 25 °C even larger values of ca. 64 bar were obtained. It is likely that the sharply rheopectic behaviour at 25 °C shown in Figure 4.1 (within the first minute of applied shear) would also be detected for the sample sheared at 25 °C in Figure 7.5 if data had been collected within the first minute of applied shear.

7.2.1.5 Cryo-SEM Results – Sodium Sulfate Sheared at Various Temperatures with High-Active LAS

The rheological response observed for samples of high-active LAS sheared both without added salts and with sodium sulfate at different shearing temperatures were compared in Section 7.2.1.4. The similar rheological response obtained for the different samples implies that similar microstructures are also present; this will be examined by comparing cryo-SEM images.

In Figure 7.6, cryo-SEM images are shown for samples of high-active LAS sheared with sodium sulfate for 60 minutes in the MPR using standard processing parameters at (a) 25 °C, (b) 40 °C and (c) 75 °C. The sample sheared at 25 °C consists of a tightly-packed MLV microstructure whereas the sample sheared at 40 °C has a microstructure that is not so distinct or well-defined. It is possible that a number of MLV microstructures are also present in the sample sheared at
40 °C, although they are not as tightly-packed or as spherical as the structures formed at 25 °C. In comparison to the sample sheared at 75 °C, samples sheared at 25 °C and 40 °C do not possess microstructures consisting of significant proportions of planar lamellae.

The cryo-SEM images for high-active LAS sheared without added salts at temperatures corresponding to those displayed in Figures 7.6 (a), (b) and (c) are shown in Figures 4.5 (a), (b) and (d); similar microstructures can be observed at the various processing temperatures. It is interesting to note that in the tightly-packed MLV microstructures that form at 25 °C (shown in Figures 4.5 (a) and 7.6 (a)), the MLVs are not as spherical as those found in pastes where the MLVs form at 60 °C with added salts (e.g. Figure 5.4). A feature that is common to both Figures 7.6 (a) and (b) is the ‘webbing’ which appears to exist between the MLVs, holding them together; in Figures 4.5 (a), (b) and (c) some evidence of similar features between the MLVs are also present. It is possible that this ‘webbing’ is similar to the network of bilayers connecting the MLVs in the AOT/brine system discussed by Léon et al. (2000).

7.2.1.6 Discussion

From the results that have been presented, sodium sulfate and sodium sulfite salts appear to have no effect on the rheological behaviour or the microstructure of high-active LAS when sheared. A possible reason for this might be the similarity of the sulfate and sulfite ions to the sulfonate groups on the LAS molecules and also that the LAS system already has sodium ions present. Increasing the concentrations of these ions may not significantly change the relative concentrations of components in the LAS system, thus the balance of forces in the system would remain intact and may account for the behaviour which is similar to that exhibited by high-active LAS sheared without added salts. From further experiments conducted at 60 °C, it has also been observed that potassium sulfate does not have an effect on the response of high-active LAS when sheared.
7.2.2 Effect of Mixtures of Sodium Chloride and Sodium Sulfate on High-Active LAS with Shear at 60 °C

In Section 7.2.1, the addition of sodium sulfate (Na₂SO₄) to high-active LAS was not seen to have a significant effect on its behaviour during shear at 60 °C. This was in contrast to the salts identified in Chapter 5, such as sodium chloride, which were able to induce the formation of MLVs at 60 °C with shear. In the current section, results from shearing high-active LAS at 60 °C with mixtures of sodium chloride and sodium sulfate (salts that have been shown to affect LAS differently) will be presented and discussed. For each experiment, a total of 0.034 mol of sodium ions was added to 20 g high-active LAS with the following proportions of salts used within the salt mixtures: (1) NaCl(20%):Na₂SO₄(80%) and (2) NaCl(80%):Na₂SO₄(20%), where the percentages are given on a Na⁺ mol-% basis.

7.2.2.1 Rheological Results from the MPR

The typical rheological response (ΔPₚ versus processing time) obtained from shearing high-active LAS at 60 °C with salt mixtures of sodium chloride and sodium sulfate can be seen in Figure 7.1, where the 90 % confidence intervals (from the Student’s t-distribution) for ΔPₚ values are shown at 60 minutes of shear. It is evident that when samples of high-active LAS are sheared with the salt mixtures containing different proportions of sodium chloride and sodium sulfate at 60 °C, a similar rheological response is observed. During the first 10 minutes of shear in the MPR, the samples exhibit strongly rheopectic behaviour, this is followed by weakly rheopectic behaviour leading to rheological steady state. After 60 minutes of shear, the values of ΔPₚ are not significantly different, indicating that the paste samples are of a similar level of firmness.

In comparison with the rheological response of high-active LAS sheared with 10 wt. % sodium chloride at 60 °C which is shown in Figure 5.6, both the rheopectic response and magnitude of ΔPₚ values are similar for paste samples sheared with either of the salt mixtures studied. From the rheological results presented, it is reasonable to expect that the samples sheared with the salt mixtures will possess tightly-packed MLV microstructures similar to the microstructure observed for high-active LAS sheared with 10 wt % sodium.
chloride at 60 ºC. Evidence for these microstructures will be discussed in Sections 7.2.2.2 and 7.2.2.3.

7.2.2.2 X-ray Diffraction Results

◊ Orientation of Microstructure

Typical graphs of X-ray intensity versus azimuthal angle, $\chi$, are presented in Figure 7.7 for high-active LAS sheared with (a) NaCl(20%):Na₂SO₄(80%) and (b) NaCl(80%):Na₂SO₄(20%). These X-ray diffraction measurements were obtained during shearing experiments in the MPR at 60 ºC using standard processing parameters. Data are shown prior to shear where the sample was compressed to 4 bar, and after 20 and 50 minutes of shear; results are plotted as continuous lines and shifted along the y-axis for clarity.

Figures 7.7 (a) and (b) show orientation profiles that are typical for high-active LAS samples forming MLV microstructures with shear from samples with aligned planar lamellae. The compressed samples exhibit peaks of X-ray intensity at $\chi = 90^\circ$ and $270^\circ$. With shear, the X-ray intensity is evenly distributed about values of $\chi$ and the peaks disappear. This type of behaviour is expected from the rheological response previously observed in Section 7.2.2.1.

◊ Length of the Characteristic Repeating Microstructure Unit (d-spacing)

In Figure 7.3, the d-spacing values obtained at steady state (where the d-spacing remains constant over time at a given shear rate) are shown for high-active LAS sheared at 60 ºC in the MPR with mixtures of sodium chloride and sodium sulfate salts. To give an indication of the errors, the 90% confidence intervals (calculated from the Student’s $t$-distribution) have been included; results from shearing high-active LAS without added salts at 60 ºC are shown for comparison. It can be seen that the d-spacing results are not significantly different for high-active LAS sheared with either of the salt mixtures at 60 ºC. In addition, the d-spacing values (and thus the bilayer repeat distances) in samples sheared with the salt mixtures are not significantly different from those obtained from high-active LAS sheared without added salts at 60 ºC.
7.2.2.3  Cryo-SEM Results

Typical cryo-SEM images obtained for samples of high-active LAS at 60 °C sheared for 60 minutes with mixtures of sodium chloride and sodium sulfate salts are shown in Figure 7.8. These images confirm the presence of tightly-packed MLV microstructures in the pastes sheared with both the salt mixtures that were investigated. The MLVs in Figures 7.8 (a) and (b) appear spherical, of a similar average size (ca. 350 nm) and fairly narrow size distribution. When compared to the microstructure obtained when high-active LAS is sheared with 10 wt. % sodium chloride at 60 °C (see Figure 5.9 (b)), no difference can be perceived.

7.2.2.4  Discussion

The results presented in this section were obtained from experiments where the effect of shearing high-active LAS at 60 °C with mixtures of salts was investigated. For the salt mixtures of sodium chloride and sodium sulfate that were used in the experiments, varying the proportion of sodium chloride to sodium sulfate in the mixture did not appear to affect the behaviour of high-active LAS with shear. It is likely that, as discussed in Section 7.2.1.6, the added sodium sulfate salts were not of a significant enough concentration to affect the shear-induced behaviour of high-active LAS. Indeed, the behaviour that was exhibited was similar to that shown by samples sheared with sodium chloride alone (Chapter 5). It is not then surprising that the salt mixture with the lower proportion of sodium chloride (20 mol-% basis of added Na⁺) was sufficient to induce the MLV microstructure with shear, as a lower amount of sodium chloride (1 wt. %) has been shown to induce MLVs previously in Section 5.1.3.

7.2.3  Effect of Tri-Ammonium Citrate and Sodium Hydroxide on High-Active LAS with Shear at 60 °C

In this section of Chapter 7, unusual microstructures obtained from shearing high-active LAS at 60 °C with tri-ammonium citrate and sodium hydroxide are examined.
7.2.3.1 Rheological Results from the MPR

Figure 7.1 shows the typical rheological response ($\Delta P_p$ versus processing time) of high-active LAS sheared with tri-ammonium citrate and sodium hydroxide at $60^\circ$C; the 90% confidence intervals for $\Delta P_p$ values (calculated from the Student’s $t$-distribution) are included at 60 minutes of shear. From this graph, high-active LAS sheared with tri-ammonium citrate appears to reach rheological steady state (with $\Delta P_p$ values of ca. 28 bar) almost immediately with shear. The rheological behaviour of high-active LAS with sodium hydroxide is more erratic and variable; this is evident in a much wider 90% confidence interval for $\Delta P_p$ at 60 minutes. The results that are shown for shearing high-active LAS with sodium hydroxide display thixotropic behaviour (where $\Delta P_p$ values decrease) before steady state is reached; for some samples, a brief period of sharply rheopectic behaviour was also observed prior to the thixotropic response.

7.2.3.2 X-ray Diffraction Results

In this section instead of presenting or ientation profiles (i.e. graphs of X-ray intensity versus azimuthal angle, $\chi$), X-ray scattering patterns (Figure 7.9) are used to describe the orientation of microstructures present in the sheared samples. Also, diffraction profiles (graphs of X-ray intensity versus scattering angle, $2\theta$) will be shown to better compare the length of the characteristic repeating microstructure unit (d-spacing) between the samples.

◊ Orientation of Microstructure

Figure 7.9 shows the typical X-ray scattering patterns obtained during shearing experiments for high-active LAS in the MPR using standard processing parameters. Results are displayed for (a) high-active LAS sheared without added salts at $25^\circ$C, (b) high-active LAS sheared with tri-ammonium citrate at $60^\circ$C and (c) high-active LAS with sodium hydroxide at $60^\circ$C. The sample sheared at $25^\circ$C is shown for reference; its X-ray scattering pattern is a ring of evenly distributed X-ray intensity corresponding to a d-spacing of ca. 30 Å. In Figure 7.9, X-ray scattering patterns are displayed (i) immediately after sample compression to 4 bar, prior to shear; and at the following intervals after the commencement of shear: (ii) 0 minutes, (iii) 20 minutes and (iv) 50 minutes.
The results for high-active LAS sheared with tri-ammonium citrate at 60 °C are shown in Figure 7.9 (b). Instead of only one diffraction ring appearing, as in the case for high-active LAS sheared without added salts at 25 °C (Figure 7.9 (a)) and in the samples discussed in Chapters 4 and 5, two diffraction rings are present. The outer ring in Figure 7.9 (b) is of a similar scattering angle 2θ (and d-spacing value) to the ring that is observed in Figure 7.9 (a). With shear, an X-ray diffraction ring where the X-ray intensity is evenly distributed is formed in Figure 7.9 (a), however the distribution of X-ray intensity is not evenly distributed about the outer ring in Figure 7.9 (b) and appears more intense about the equator (χ = 90°, 270°). The inner diffraction ring that is observed in Figure 7.9 (b) appears more distinct during sample compression prior to shear, though it is still detected after shearing for 50 minutes. Although the inner diffraction ring appears to have an even distribution of X-ray intensity, additional X-ray scattering from the carbon-fibre capillary is also detected around this region of interest and is difficult to separate from the scattering due to the sample.

In Figure 7.9 (c), the X-ray scattering patterns for high-active LAS sheared at 60 °C with sodium hydroxide are shown. Like the scattering patterns shown in Figure 7.9 (b), the scattering patterns in Figure 7.9 (c) consist of more than one diffraction ring. The outermost diffraction ring occurs at a similar scattering angle to the outer rings that were discussed in Figures 7.9 (a) and (b), and like the outer ring that appears in Figure (b), the X-ray intensity is also greatest about the equator. The innermost diffraction ring appears as the sample is sheared and it is clear that the intensity of this diffraction ring is greatest about the equator. In addition to the innermost and outermost diffraction rings in Figure 7.9 (c), there is some evidence (though faint) for an intermediate diffraction ring with increased intensity about the equator, corresponding to a d-spacing of ca. 34 Å. McKeown (2001) also observed this in experiments with the X-ray beam path directed in the side-capillary position. These results were attributed to the alignment of planar bilayers parallel to the plane of the capillary wall and adjacent to it, with a larger inter-lamellar distance (ca. 34 Å) than in the bulk of the sample (ca. 30 Å).
Length of the Characteristic Repeating Microstructure Unit (d-spacing)

In Figure 7.10, typical X-ray diffraction profiles are shown for high-active LAS in the MPR using standard processing parameters at (a) sample compression to 4 bar prior to shear and (b) after 50 minutes of shear. Results are displayed for high-active LAS sheared without added salts at 25 °C, and at 60 °C with tri-ammonium citrate and sodium hydroxide.

The diffraction profiles for the compressed samples (Figure 7.10 (a)) are similar to the profiles in Figure 7.10 (b) obtained after 50 minutes of shear. However, there are some differences. Firstly, for high-active LAS sheared with tri-ammonium citrate, the diffraction peak occurring at ca. 1.4° 2θ in Figure 7.10 (a) appears more distinct than the corresponding peak in Figure 7.10 (b). As this peak corresponds to the inner ring seen in Figure 7.9 (b), the earlier comment that the inner ring appeared more distinct in Figure 7.9 (b-i) than in (b-ii) is justified.

The other difference occurs in the diffraction profile for high-active LAS sheared with sodium hydroxide. In this case, the intensity of the diffraction peak at ca. 2.1° 2θ for the compressed sample (corresponding to the innermost ring in Figure 7.9 (c)) increases with shear at the expense of the intensity of the diffraction peak occurring at ca. 2.9° 2θ (the outermost ring in Figure 7.9 (c)).

From the X-ray scattering patterns in Figure 7.9, the outermost diffraction rings obtained from the different samples in Figures 7.9 (b) and (c) appear in the same region as the single ring that appears in Figure 7.9 (a). Analysis of Figure 7.10 (b) with the Bragg equation (Appendix C, Equation C.7) generates the following d-spacing results: 30 Å for high-active LAS sheared at 25 °C, 32 Å for high-active LAS sheared at 60 °C with tri-ammonium citrate and 30 Å for high-active LAS sheared at 60 °C with sodium hydroxide. The innermost diffraction rings observed after 50 minutes of shear in Figures 7.9 (b-iv) and (c-iv) correspond to d-spacing values of ca. 59 Å and 42 Å respectively, from the diffraction peaks that appear in Figure 7.10 (b). In repeated experiments shearing high-active LAS with tri-ammonium citrate and sodium hydroxide, the d-spacing values obtained for the inner diffraction rings have been highly variable ranging from ca. 52 to 59 Å and ca. 40 to 52 Å, respectively.
7.2.3.3 Cryo-SEM Results

The cryo-SEM images that will first be discussed in this section refer to high-active LAS samples sheared at 60 °C in the MPR using standard processing conditions for 30 minutes with tri-ammonium citrate and 60 minutes with sodium hydroxide (Figures 7.11 and 7.12 respectively). For clarity, the images are shown under different magnifications to highlight salient features. Following the discussion of these figures, additional points will be raised with cryo-SEM images of further samples of high-active LAS sheared with tri-ammonium citrate at 60 °C for illustration (Figures 7.13 and 7.14).

Shearing high-active LAS at 60 °C with tri-ammonium citrate results in what appears to be a biphasic microstructure. The two types of microstructure are shown co-existing in Figure 7.11 (a-ii) and each at greater detail in Figures 7.11 (b) and (c). The location of images (a-ii), (b) and (c) within the cross-section of the extrudate sample can be ascertained from Figure 7.11 (a-i). In these images, the most striking feature is the presence of large worm-like structures. A close-up view of a ‘worm’ in Figure 7.11 (a-ii) is shown in Figure 7.11 (b). In this sample, the worm-like structures have a typical length of ca. 100 µm and breadth of ca. 10 µm. The remainder of the sample microstructure consists of much smaller MLV-like structures in a tightly-packed arrangement, shown in Figure 7.11 (c). However, the MLVs do not appear as distinctly formed as in the MLV-rich samples previously discussed in Chapters 4 and 5, though the size of the MLVs are in the same order of magnitude. From Figures 7.11 (a-i) and (a-ii), the shear-induced orientation of the worm-like structures can be observed. The green dotted lines indicate the length-wise orientation of the worm-like structures in relation to the edge of the capillary wall. However it is not known how these structures are arranged along the length of the capillary.

In Figure 7.12, the cryo-SEM images of a high-active LAS sample sheared at 60 °C with sodium hydroxide in the MPR under standard processing parameters for 60 minutes are shown. Although the images are not as clear as in Figure 7.11 for high-active LAS sheared with tri-ammonium chloride, the sample appears to possess a similar biphasic microstructure. The worm-like structures in Figures 7.12 (a) and (b) are shown aligned in relation to the capillary wall. As in Figure
7.11, green dotted lines are used to indicate the orientation of these structures. A detailed view of a ‘worm’ in Figure 7.12 (a-ii) is shown in Figure 7.12 (c). The width of a typical ‘worm’ in this sample is ca. 15 µm, which is greater than that observed for similar structures in Figure 7.11. Common features of the worm-like structures that appear in both samples are the horizontal ridges that appear across the width of the ‘worms’. In Figure 7.12 (d), an image that is representative of the remaining microstructure is shown. Although MLV-like microstructures are present in Figure 7.12 (d), they do not form a tightly-packed MLV microstructure. Instead, the microstructure is similar to that in Figure 7.4 for samples of high-active LAS sheared at 60 °C with sodium sulfate and sodium sulfite.

The sample microstructure shown in Figure 7.11 was obtained after shearing high-active LAS at 60 °C with tri-ammonium citrate for 30 minutes in the MPR. For that particular sample the biphasic nature of the microstructure was well-defined: worm-like structures were clearly orientated within the MLV-rich microstructure that was also present. However, repeated experiments resulted in samples with slightly different microstructural features even though the rheological response and X-ray diffraction data obtained were similar to the results displayed in Figures 7.1 and 7.9 (b). The following discussion will focus on the cryo-SEM images in Figures 7.13 and 7.14 obtained from further samples of high-active LAS sheared for 30 minutes at 60 °C with tri-ammonium citrate.

In Figure 7.13, the biphasic microstructure that was first discussed in Figure 7.11 can be seen. A worm-like structure is present in Figure 7.13 (a-i), although it is much larger than the similar structures seen in Figures 7.11 and 7.12. A close-up view of the ‘worm’ is shown in Figure 7.13 (a-ii) where the horizontal ridges across the width of the worm-like structure can be seen more clearly in addition to the MLV-rich microstructure co-existing with it. The worm-like structures were observed joining together with other ‘worms’; evidence for this is shown in Figure 7.13 (b) where the pink dotted lines emphasize the cross-over point between separate worm-like structures. In addition, areas that were clearly biphasic, though not consisting of defined worm-like structures, were observed: an example is presented in Figure 7.13 (c), where a solid yellow line separates
two distinct microstructural regions. The appearance of the region rich in worm-like structures is suggestive of planar lamellae.

The cryo-SEM images for the final sample of high-active LAS sheared at 60 °C for 30 minutes with tri-ammonium citrate are shown in Figure 7.14. Instead of the clearly biphasic microstructures that have been observed for the other samples consisting of the same materials (Figures 7.11 and 7.13), the microstructure that is present in this sample appears to be comprised of one phase only. This phase consists of MLVs that seem to be dispersed throughout some sort of matrix medium; Figures 7.14 (a) and (b) show the phase at different magnifications. It is likely that this MLV-rich phase is very similar to the MLV-rich phases seen in Figures 7.11 (c) and 7.13.

7.2.3.4 Discussion

In this section the results from shearing high-active LAS with tri-ammonium citrate and sodium hydroxide salts at 60 °C were presented. As shown in the X-ray diffraction data presented in Figures 7.9 (b) and (c), samples sheared with these salts result in microstructures that exhibit an ‘inner’ X-ray diffraction ring that is not present for any of the other samples discussed in Chapters 4 and 5. This inner diffraction ring corresponds to a microstructural repeat distance of between ca. 40 to ca. 59 Å, larger than the standard lamellar repeat distance of ca. 30 Å. This additional diffraction ring appears to be associated with the biphasic microstructures that have been observed for the samples sheared with tri-ammonium citrate and sodium hydroxide.

The biphasic microstructures created with tri-ammonium citrate (Figures 7.11, 7.13 and 7.14) are interesting. In particular, it is surprising that the supposedly monophasic microstructure in Figure 7.14, while exhibiting the same rheological response and X-ray diffraction data during experiments, is different from the clearly biphasic microstructure contained in Figure 7.11. It is possible though, that the microstructure present in Figure 7.14 consists of MLVs dispersed throughout a matrix of a different phase and that phase separation occurs with shear to create worm-like structures that become orientated with shear. With further shearing, the worm-like structures interact and join together with other ‘worms’ thus creating separate regions of MLV-rich and ‘worm’-rich phases.
Although the samples in Figures 7.11, 7.13 and 7.14 were subject to the same duration of shear, it is likely that the variation in microstructure that is observed is due to the inconsistencies introduced in the sample preparation stage prior to loading into the MPR.

The phenomenon of shear-induced phase separation has also been observed for low concentration worm-like micellar solutions (Keller et al., 1998). Although the term ‘worm-like structures’ has been used in reference to the new structures observed with high-active LAS, such as that pictured in Figure 7.11 (b), these structures should not be confused with ‘worm-like micelles’. Worm-like micelles, like liquid crystalline materials, are also formed by surfactant self-assembly. However worm-like micelles are much smaller than the worm-like structures that were identified in this section. Typically, the diameter of a worm-like micelle is ca. 5 nm, with a length of a few microns; in dilute systems, worm-like micelles of a greater length (>1 µm) are formed. The large worm-like structures presented in this chapter have, to the best of the author’s knowledge, not been previously reported in the literature.

It is likely that the interaction of high-active LAS with the tri-ammonium citrate and sodium hydroxide salts during shear at 60 ºC is important in the formation of the biphasic microstructures that result, with the nature of the added ions being a key factor. From the results that have been presented previously, additional sodium (Na⁺) ions do not appear to affect the microstructures that result from shearing high-active LAS at 60 ºC: shearing with sodium chloride has resulted in an MLV-rich microstructure evolving whereas shearing with sodium sulfate has no effect. In the case of experiments with sodium hydroxide, the implication is that the hydroxyl (OH⁻) ions play an important role in creating the biphasic microstructure present in the resultant paste. However, with the tri-ammonium citrate salt ((NH₄)₃C₆H₅O₇), it is not clear which of the ions has a greater role in the creation of the biphasic microstructure. Previous experiments shearing high-active LAS with sodium citrate (Na₃C₆H₅O₇*2H₂O) have resulted in samples with tightly-packed MLV microstructures (see Chapter 5). Given the biphasic nature of the sample processed with tri-ammonium citrate, the implication is that the ammonium (NH₄⁺) ion is more likely to contribute to this type of biphasic microstructure as we have argued that the sodium ion has no effect. However,
previous results have shown that an MLV-rich microstructure evolves when ammonium chloride is sheared with high-active LAS. Given that shearing samples with sodium chloride also produces MLV-rich microstructures, this would imply that the ammonium ion has less effect than the chloride (Cl\(^-\)) ion on the shear-induced microstructures that result. It is therefore likely that the shear-induced microstructures that arise when high-active LAS is sheared with various salts (e.g. MLVs, biphasic microstructures) are not dependent on a single species of ion of either positive or negative charge, but on the combined effect of all the ionic species present.

7.3 Chapter Summary

Sodium sulfate and sodium sulfite salts did not have an effect on the shear-induced behaviour of high-active LAS at 60 °C. When sodium sulfate was used together with sodium chloride, tightly-packed MLV microstructures were formed due to the sodium chloride; again the sodium sulfate had no effect. The use of tri-ammonium citrate and sodium hydroxide salts resulted in a biphasic microstructure forming with shear: an MLV-rich phase and a phase of worm-like structures. These worm-like structures exhibit shear-induced orientation and have not been previously seen in the literature. From the results in this chapter and those presented in previous chapters, it is likely that the shear-induced microstructures that form in high-active LAS at 60 °C are dependent on the combination of negatively and positively-charged ions that are added during shear.
Figure 7.1. Typical response of high-active LAS sheared with various salts in the MPR using standard processing parameters at 60 °C; the pseudo-steady state pressure difference, $\Delta P_p$, is plotted against processing time. The proportion of salt(s) to LAS was fixed by adding 0.034 mol of Na$^+$ or NH$_4^+$ through the salt (or salt mixture) to 20 g of high-active LAS and the ratio of salts within the salt mixtures was calculated on a Na$^+$ mol-% basis. The 90 % confidence intervals for $\Delta P_p$ (calculated using the Student’s $t$-distribution) are shown at 60 minutes of processing time.
Figure 7.2. X-ray intensity versus azimuthal angle, $\chi$, for high-active LAS sheared at 60 °C in the MPR using standard processing parameters with (a) sodium sulfate and (b) sodium sulfite. The proportion of salt to LAS was fixed by adding 0.034 mol of Na$^+$ to 20 g of high-active LAS. Data are shown prior to shear (i.e. sample compressed to 4 bar) and after 20 and 50 minutes of shear. The data series are plotted as continuous lines and shifted along the y-axis for clarity.
Figure 7.3. Steady state X-ray d-spacing values obtained from high-active LAS paste samples during shear in the MPR using standard processing parameters. Results are shown for LAS sheared at 60°C with various salts (or salt mixtures) where the proportion of salt(s) to LAS was fixed by adding 0.034 mol of Na⁺ to 20 g of high-active LAS and the ratio of salts within the salt mixtures was calculated on a Na⁺ mol-% basis. The 90% confidence intervals for X-ray d-spacing values (calculated using the Student’s t-distribution) are shown.
Figure 7.4. Cryo-SEM images of high-active LAS sheared for 60 minutes in the MPR using standard processing parameters with (a) sodium sulfate at 75 °C and (b) sodium sulfite at 60 °C. The proportion of salt to LAS was fixed by adding 0.034 mol of Na⁺ to 20 g of high-active LAS. From (i) to (ii), the images are shown at decreasing magnification.
Figure 7.5. Typical response of high-active LAS sheared with sodium sulfate in the MPR using standard processing parameters at various temperatures. The pseudo-steady state pressure difference, $\Delta P_p$, is plotted against processing time. The proportion of salt to LAS was fixed by adding 0.034 mol of Na$^+$ to 20 g of high-active LAS. The 90% confidence intervals for $\Delta P_p$ (calculated using the Student’s $t$-distribution) are shown at 60 minutes of processing time.
Figure 7.6. Cryo-SEM images of high-active LAS sheared for 60 minutes in the MPR using standard processing parameters with sodium sulfate at (a) 25 °C, (b) 40 °C and (c) 75 °C. The proportion of salt to LAS was fixed by adding 0.034 mol of Na\(^+\) to 20 g of high-active LAS.
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Figure 7.7. X-ray intensity versus azimuthal angle, $\chi$, for high-active LAS sheared at 60 °C in the MPR using standard processing parameters with the following salt mixtures: (a) sodium chloride (20%) to sodium sulfate (80%) and (b) sodium chloride (80%) to sodium sulfate (20%). The proportion of salts to LAS was fixed by adding a total of 0.034 mol of Na$^+$ to 20 g of high-active LAS and the ratio of salts within the salt mixtures was calculated on a Na$^+$ mol-% basis. Data are shown prior to shear (i.e. sample compressed to 4 bar) and after 20 and 50 minutes of shear. The data series are plotted as continuous lines and shifted along the y-axis for clarity.
Figure 7.8. Cryo-SEM images for high-active LAS sheared at 60 °C in the MPR using standard processing parameters with the following salt mixtures: (a) sodium chloride (20%) to sodium sulfate (80%) and (b) sodium chloride (80%) to sodium sulfate (20%). The proportion of salts to LAS was fixed by adding a total of 0.034 mol of Na\(^+\) to 20 g of high-active LAS and the ratio of salts within the salt mixtures was calculated on a Na\(^+\) mol-% basis.
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Figure 7.9. X-ray scattering patterns obtained during shearing experiments for high-active LAS in the MPR using standard processing parameters. Results are shown for: (a) high-active LAS without added salts at 25 °C, (b) high-active LAS with tri-ammonium citrate at 60 °C and (c) high-active LAS with sodium hydroxide at 60 °C. Measurements were taken: (i) during sample compression to 4 bar prior to shear; and at the following intervals after the commencement of shear: (ii) 0 minutes, (iii) 20 minutes and (iv) 50 minutes. The proportion of salt to LAS was fixed by adding 0.034 mol of Na⁺ or NH₄⁺ to 20 g of high-active LAS.
Figure 7.10. X-ray diffraction profiles obtained during shearing experiments for high-active LAS in the MPR using standard processing parameters. Results are shown for high-active LAS sheared at 25 °C without added salts, at 60 °C with tri-ammonium citrate and 60 °C with sodium hydroxide. The X-ray diffraction profiles are shown: (a) prior to shear (during sample compression to 4 bar) and (b) after 50 minutes of shear. The proportion of salt to LAS was fixed by adding 0.034 mol of Na⁺ or NH₄⁺ to 20 g of high-active LAS.
Figure 7.11. Cryo-SEM images of high-active LAS sheared for 30 minutes with tri-ammonium citrate at 60 °C in the MPR using standard processing parameters (sample 1). The proportion of salt to LAS was fixed by adding 0.034 mol of NH₄⁺ to 20 g of high-active LAS. The images (a), (b) and (c) are shown at different magnifications to highlight different microstructural features; (a-i) shows schematically the approximate placement of (a-ii) in relation to the circular cross-section of the extrudate.
Figure 7.12. Cryo-SEM images of high-active LAS sheared for 60 minutes with sodium hydroxide at 60 ºC in the MPR using standard processing parameters. The proportion of salt to LAS was fixed by adding 0.034 mol of Na+ to 20 g of high-active LAS. The images (a), (b), (c) and (d) are shown at different magnifications to highlight different microstructural features; (a-i) and (b-i) show schematically the approximate placements of (a-ii) and (b-ii) respectively, in relation to the circular cross-section of the extrudate.
Figure 7.13. Cryo-SEM images of high-active LAS sheared for 30 minutes with tri-ammonium citrate at 60 °C in the MPR using standard processing parameters (sample 2). The proportion of salt to LAS was fixed by adding 0.034 mol of Na⁺ to 20 g of high-active LAS. The images (a-i), and (a-ii) show a ‘worm’ at different magnifications. Image (b) shows the cross-over point between two ‘worms’, highlighted by the dotted lines and (c) shows the biphasic nature of the microstructure, with the yellow line separating the different microstructures.
Figure 7.14. Cryo-SEM images of high-active LAS sheared for 30 minutes with tri-ammonium citrate at 60 °C in the MPR using standard processing parameters (sample 3). The proportion of salt to LAS was fixed by adding 0.034 mol of Na⁺ to 20 g of high-active LAS. The images (a) and (b) show the MLV-containing microstructure at different magnifications.
Chapter 8

Conclusions and Recommendations for Future Work

Concentrated compact detergent powders are an important product for the detergent industry. To cope with the demand for powders with high bulk densities and high active matter contents, alternative manufacturing routes to the traditional spray-drying methods are used by detergent manufacturers. Surfactant agglomeration is one such route used by major manufacturers of compact detergent powders. Prior to agglomeration, a paste-structuring stage is often used to modify the physical properties of the concentrated paste-like surfactant-based systems that are used. This is to ensure that the surfactant paste is of a suitable consistency for the agglomeration process and to enable high levels of surfactant, or active matter, to be incorporated into the detergent granules. Surfactant pastes with successfully modified properties are deemed ‘structured’.

Despite the importance of the paste-structuring process, it is poorly understood. There is a particular lack of understanding when the surfactant LAS is used. Although the global consumption of LAS is worth billions of pounds every year, there has been little scientific data published on it. As outlined in Chapter 2, the high-active LAS used in the detergent industry exists as a mixture of LAS isomers and its composition can vary slightly depending on the application it is used for. With this in mind, it is understandable why so few scientific studies have been performed. The industrial approach to improvements and developments in paste-structuring with high-active LAS has therefore been based on trial-and-error.

The aim of this work has been to contribute to the scientific understanding of paste-structuring with high-active LAS. The approach has focussed on studying
the effect of added salts on the microstructure and rheological behaviour of high-active LAS with shear and relating this to paste-structuring.

In the concluding chapter of this thesis, there are three main sections. The first section will summarise the experimental results from this work. In the section that follows, the contributions from this work to science and industry will be discussed. Finally, in the third section, recommendations for future work will be made.

### 8.1 Summary of Experimental Results

Following the work of McKeown (2001), the Cambridge Multi-Pass Rheometer (MPR) was used as a simplified extrusion system. Twin-screw extrusion is used in industry. Throughout this work the shearing parameters in the MPR were kept constant; this allowed the reproducible application of shear to samples of high-active LAS. The experiments were conducted using a wide range of salts that were sheared with high-active LAS. While the industrially relevant processing temperature of 60 °C was ordinarily used, other process temperatures were also investigated. During experiments, both rheological and X-ray diffraction data were obtained. The rheological data, consisting of values of $\Delta P_p$, provided a measure of the firmness of the sheared paste samples and an indication of whether the pastes were ‘structured’. After the samples were sheared, cryo-SEM observations were made.

#### 8.1.1 Sodium Disilicate – an Industrial Structuring Agent

In Chapter 4, the effect of shearing high-active LAS with an industrial structuring agent, sodium disilicate, was examined. Experiments were carried out at different temperatures and the results were compared with those obtained from shearing high-active LAS without added salts. The following results were observed.

i) At elevated temperatures (40, 60 and 75 °C), samples of high-active LAS sheared without added salts possessed microstructures consisting largely of planar bilayers. However at 25 °C, tightly-packed MLV microstructures were formed (ca. 700 nm in diameter).
ii) At all the temperatures that were investigated (25, 40, 60 and 75 °C), the addition of sodium disilicate (10 wt.%) resulted in the formation of tightly-packed MLVs within the microstructure of high-active LAS. The MLVs were ca. 50-500 nm in diameter, depending on the processing conditions.

iii) Samples consisting of tightly-packed MLV microstructures exhibited rheopectic behaviour. The sheared paste samples were firm and appeared ‘structured’.

iv) Samples consisting of planar bilayers exhibited time-independent rheological behaviour. The sheared paste samples were soft and, by visual and manual inspection, appeared ‘structured’.

v) The sodium disilicate appeared to reduce the bilayer repeat distance in high-active LAS.

8.1.2 Further Salts Inducing MLVs With Shear

In Chapter 5, results were presented for a wide variety of salts that were shown to induce MLVs with shear in high-active LAS at elevated temperatures. Experiments were carried out to compare the microstructure and rheological behaviour of high-active LAS sheared with the various salts at 60 °C. Following this, sodium chloride was selected as a model salt and the effect of processing temperature was examined for comparison with those obtained using the industrial structuring agent, sodium disilicate. Finally the effect of changing the concentration of sodium chloride was also examined. In summary, the results that were obtained are listed below.

i) At 60 °C, a variety of salts were found to induce the formation of tightly-packed MLVs in high-active LAS with shear. This was accompanied by rheopectic behaviour. These salts include ammonium chloride, sodium chloride, sodium citrate dihydrate, sodium disilicate, sodium nitrate, sodium phosphate dodecahydrate, sodium phosphate monohydrate, tetramethyl-ammonium chloride and tetramethyl-ammonium nitrate.
Chapter 8: Conclusions and Recommendations for Future Work

ii) The size and size distribution of MLVs varied depending on the salt added, and were related to the firmness exhibited by the sheared pastes.

iii) The repeat distance of the bilayers within the MLVs was not related to the level of paste firmness.

iv) Salts containing associated water molecules increased the bilayer repeat distance of high-active LAS.

v) Salts consisting of both bulky anions and cations increased the bilayer repeat distance of high-active LAS.

vi) At elevated processing temperatures (40, 60, and 75 °C), sodium chloride (10 wt. %) proved as effective as the industrial structuring agent, sodium disilicate, in creating firm sheared pastes and comparable MLV microstructures. No change in the bilayer repeat distance was observed with sodium chloride.

vii) A lower proportion of sodium chloride (1 wt. %) was, over time, as effective in producing sheared pastes of comparable firmness and MLV microstructure. The lower proportion of sodium chloride resulted in an initial delay in rheopectic behaviour.

8.1.3 Effect of Time on MLV Formation and Stability

In Chapter 6, the results were presented in two parts. Firstly, the effect of the duration of shear on MLV size was examined. Secondly, the stability of MLVs without shear was studied and the effects of added salts and processing temperature on this stability were examined. The results that were obtained are summarised below.

i) The formation of MLVs is a time-dependent process.

ii) MLV formation begins from an aligned planar lamellar state; with shear, MLVs form between the aligned lamellae and a biphasic structure exists.

iii) A longer duration of shear produces MLVs that are more spherical and uniform in size and also smaller on average.
iv) MLVs are metastable in the absence of shear. They revert back to planar lamellae with time, forming ‘lamellar clusters’ throughout the paste.

v) Pastes where ‘lamellar clusters’ have formed are less firm than pastes without such structures.

vi) MLV stability is affected by the processing temperature and salts added during the shearing process.

8.1.4 Salts Inducing Non-MLV Microstructures With Shear

In Chapter 7, results for salts which have been identified as producing non-MLV microstructures when sheared with high-active LAS at 60 °C were presented. The results were discussed in three main sections. Firstly, results were shown for salts (sodium sulfate and sodium sulfite) that did not have a significant effect when sheared with high-active LAS at 60 °C. Secondly, mixtures of sodium sulfate and sodium chloride when sheared with high-active LAS at 60 °C were studied. Finally, the effect of salts (tri-ammonium citrate and sodium hydroxide) which create large worm-like structures when sheared with high-active LAS at 60 °C was presented. The results are listed below.

i) Sodium sulfate and sodium sulfite salts, at the concentrations used in this work, did not have an effect on either the microstructure or rheological behaviour of high-active LAS when sheared at various temperatures (25, 40, 60, and 75 °C).

ii) Mixtures of sodium sulfate and sodium chloride caused high-active LAS to form MLV microstructures when sheared at 60 °C. The sodium sulfate again had no effect as the MLVs were induced with the sodium chloride.

iii) Tri-ammonium citrate and sodium hydroxide salts created biphasic microstructures when sheared with high-active LAS at 60 °C. An MLV-rich phase and phase rich in worm-like microstructures coexisted.

iv) With shear, the worm-like microstructures were orientated with respect to the capillary. Although the dimensions varied, typical worm-like structures were ca. 100 µm in length and ca. 10 µm in breadth.
8.2 Summary of Contributions

In this work, a scientific study of a commercial surfactant system has been conducted. The current section will summarise the contributions of this work to scientific knowledge and industrial practice.

8.2.1 Contributions to Scientific Knowledge

This study has resulted in a number of contributions to the scientific literature; some of this work has recently been published (Liaw and Moggridge, 2003; Liaw et al., 2003). All the contributions provide a better understanding of the shear-induced structures formed by the LAS-based surfactant system that has been studied in this work. The findings also contribute towards a better understanding of shear-induced structures, particularly MLVs, in other liquid crystalline systems. The contributions are summarised below.

i) Various MLV-inducing salts were identified. These salts were able to cause a lyotropic liquid crystalline system (existing in a planar lamellar phase) to shift to a state favouring MLV formation with shear.

ii) A link between the size and size distribution of MLVs and the firmness of the sheared material was made.

iii) Evidence was provided showing no dependency between the firmness of the sheared material and the bilayer repeat distance.

iv) The duration of shear was found to affect MLV shape, size and size distribution.

v) MLVs were shown to be metastable in the absence of shear. In addition, MLV stability was shown to be affected by added salts and processing temperature.

vi) Shear-induced phase separation was found to occur with the addition of particular salts.

vii) ‘Large’ worm-like structures were identified. These have not been reported previously in the literature.
8.2.2 Contributions to Industrial Practice

The results from this work are not only scientifically interesting, but also industrially useful. The potential contributions from this work to industrial practice are listed below.

i) ‘Structured’ firm pastes were found to possess tightly-packed MLV microstructures thus providing a scientific basis for an industrial phenomenon.

ii) The duration of shear (processing time) was identified as an important feature in determining the firmness of the surfactant paste. Another feature that could be important to industrial processing is that the greatest increase in paste firmness is often achieved at the start of the shearing process.

iii) Sodium chloride was identified as an alternative industrial structuring agent to sodium disilicate. Sodium chloride has the advantage of being cheaper than sodium disilicate.

iv) Low concentrations of added salts were found to produce pastes of comparable firmness to higher levels of salts. Although using a smaller quantity of structuring agent would be advantageous in terms of cost, the lag time in rheopectic behaviour, which is initially observed with shear, may require longer processing times to reach the desired level of firmness and this may not be desired.

v) Evidence was provided to show structured pastes becoming less firm over time. This result indicates that structured pastes should not be kept for long periods before being used.

vi) Evidence was provided which indicates that slight batch variations in the sodium sulfate content of high-active LAS should have no effect on the paste-structuring. However, slight variations of sodium chloride in the batches of high-active LAS may affect its paste-structuring behaviour.

vii) Pastes structured with sodium hydroxide or tri-ammonium citrate were found to exist in a complex biphasic microstructural arrangement and to exhibit shear-induced phase separation. Although it is possible to produce
firm pastes, it is also likely that the results obtained with these pastes are prone to greater variation due to the phase separation.

8.3 Recommendations for Future Work

This work has focussed on the effect of different salts on the behaviour of high-active LAS with shear. Due to practical limitations, only one set of processing conditions in the MPR was used. As the shear-induced behaviour of high-active LAS has been shown to be affected by the MPR piston speed or apparent wall shear rate (McKeown, 2001 and McKeown et al., 2003), it would be interesting to investigate the effect of the different salts on high-active LAS at different piston speeds. The experimental matrix could also be extended by considering different surfactant concentrations. This information would enable shear orientation diagrams such as those established by Roux and co-workers (Diat et al., 1993 and Roux et al., 1993) to be assembled, allowing for a more complete understanding of the LAS-system with shear. Further static pressures in the MPR could also be considered. This would be useful as industrial paste-structuring often occurs at pressures of up to 30 bar.

Another possibility for future work would be to model the paste-structuring process in an industrial twin-screw extruder. To properly understand and model the industrial paste-structuring process, it would be necessary to predict the amount of shear that the pastes are subjected to inside the twin-screw extruder. This shearing geometry is much more complicated than the capillary geometry used in the MPR. Such a model would also need to account for the additional shearing provided by internal devices, such as kneading blocks, which are often used to process the surfactant pastes.

From an industrial viewpoint, the paste-structuring process is only useful if detergent granules of the desired quality and surfactant concentration can be produced from structured surfactant paste. In the present work, paste firmness was associated with ‘structured’ paste, however in the industrial agglomeration process the stickiness or adhesive nature of the paste is also an important property. It is likely that this stickiness is related to the water content of the paste. It is also possible that the shear-induced structures that form can affect the
perceived stickiness of the paste. In further studies of paste-structuring it would be useful to obtain measurements of the stickiness of the sheared surfactant pastes in relation to the shear-induced structures that form. It would also be useful to be able to quantify the necessary level of paste firmness and stickiness required to produce detergent granules of the required quality and surfactant concentration.
Appendix A

A BRIEF OVERVIEW OF RHEOLOGICAL CONCEPTS

Rheology is the science of the deformation and flow of matter. It is concerned with the response of materials to an applied stress or strain. As rheological properties are important for a variety of materials, there are many relevant texts available covering a wide range of subject areas relating to rheology (e.g. food processing, polymer and composites processing, and soil mechanics). Detailed descriptions of the following rheological concepts can be found in the texts by Holland (1973), Pierce and Schoff (1982), Barnes et al., (1989), Macosko (1994) and Steffe (1996).

A.1 Some Basic Definitions

In rheological studies, materials are commonly subject to deformation by shear. The simple shear deformation of a rectangular shape is illustrated in Figure A.1. With small deformations, the angle of shear (in radians) is equal to the shear strain; both quantities are denoted by \( \gamma \).

![Figure A.1. The simple shear deformation of a rectangular shape (height \( h \) and length \( L \)) by a tangential force \( F \).](image)
The level of deformation given by the dimensionless shear strain is defined as:

$$\gamma \approx \tan (\gamma) = \frac{\Delta L}{h} \quad (A.1)$$

The rate at which the shear strain $\gamma$ varies is known as the shearing rate $\dot{\gamma}$. Simple shear deformation, such as that shown in Figure A.1, occurs when a shear stress $\tau$ acts; the tangential force $F$ divided by the area over which it is applied gives the shear stress.

For fluids, the viscosity $\eta$ is defined via:

$$\tau = \eta \dot{\gamma} \quad (A.2)$$

The viscosity can also be thought of as the ‘internal friction’ or ‘resistance to flow’ exhibited by the fluid (Barnes et al., 1989).

The corresponding quantity for solids is the shear modulus $G$, which is defined as:

$$\tau = G \gamma \quad (A.3)$$

### A.2 Classification of Fluids

Fluids can be classified according to their behaviour in simple shear flow. Ideally this can be achieved with fluid placed between two parallel plates (Figure A.2).

**Figure A.2.** Schematic diagram of a fluid in simple shear flow between two flat parallel plates. The upper plate moves at a constant velocity $U$ relative to the lower plate and the black arrows between the plates are proportional to the local velocity $v_x$ in the fluid.
Here, the shear rate $\dot{\gamma}_{yx}$ is equal to the velocity gradient in the fluid ($dv_x/dy$) which is equal to $U/h$. The shear stress $\tau_{yx}$, which causes the fluid to move in shear flow, is proportional to the velocity gradient. This is commonly expressed as Newton's law of viscosity, represented by Equation A.2.

Fluids that are considered ‘Newtonian’ have viscosities that are constant and independent of shear rate; non-Newtonian fluids have viscosities that are function of the shear rate. Newtonian viscosities may also be referred to as absolute and non-Newtonian viscosities as apparent. Non-Newtonian fluids are categorised according to the deviation in their viscosity behaviour from Newtonian fluids. This can be shown schematically in the flow curves present in Figure A.3, where shear stress $\tau$ is plotted versus shear rate $\dot{\gamma}$.

![Schematic diagram of the flow behaviour exhibited by Newtonian and various non-Newtonian fluids.](image)

**Figure A.3.** Schematic diagram of the flow behaviour exhibited by Newtonian and various non-Newtonian fluids.

### A.2.1 Non-Newtonian Fluids: Time-Independent Behaviour

We will discuss the rheological behaviour of the non-Newtonian fluids featured in Figure A.3, neglecting for the moment, any possible time dependency effects. In these cases, the apparent viscosity depends only on the steady shear rate and not the time for which the shear rate is applied.
A.2.1.1 Shear-Thinning Materials

Shear-thinning materials exhibit a decrease in the apparent viscosity with increasing shear rates (e.g. 1% aqueous solution of carrageenan gum, orange juice concentrate); such behaviour is often associated with a break-down in the microstructure of the material undergoing shear. The power law model is often used to approximate this behaviour: \( \tau \propto \dot{\gamma}^n \), where \( n \) is the power-law exponent, with \( 0 < n < 1 \).

A.2.1.2 Shear-Thickening Materials

Shear-thickening materials exhibit an increase in the apparent viscosity with increasing shear rates (e.g. concentrated cornflour solution). This type of behaviour is often associated with a rearrangement of the microstructure within the sheared material such that the resistance to flow increases with increasing shear rate. The power law model can also be used for these materials, with \( 1 < n < \infty \).

A.2.1.3 Plastic Materials

The deformation or ‘flow’ of plastic materials occurs when a critical yield stress is exceeded. Below the yield stress the material behaves as an elastic solid and Equation A.3 can be applied. This is due to its internal microstructure that is sufficiently rigid to resist stresses smaller than the yield stress. Beyond the yield stress, the material behaves as a fluid and typically exhibits flow behaviour similar to shear-thinning or Newtonian fluids (Herschel-Bulkley and Bingham plastic materials respectively).

A.2.2 Non-Newtonian Fluids: Time-Dependent Behaviour

Many of the non-Newtonian fluids mentioned in Section A.2.1 may also exhibit time-dependent effects under steady shear conditions. Fluids exhibiting time-dependent characteristics can be classed as either:

a) \textit{thixotropic} materials, where the shear stress (and apparent viscosity) decreases with time at a fixed shear rate, or
b) *rheopectic* materials, where the shear stress (and apparent viscosity) increases with time at a fixed shear rate.

It follows that *thixotropy* is time-dependent thinning and *rheopexy* is time-dependent thickening. Thixotropic materials (e.g. starch pastes, drilling muds, latex paints) are relatively common in comparison to rheopectic materials.

Causes of time-dependent behaviour include irreversible changes (e.g. cross-linking, coagulation, degradation and mechanical instability) and reversible changes (e.g. the breaking and reforming of colloidal aggregates and networks).

Experiments involving thixotropic and rheopectic materials must have a consistent, well-defined experimental procedure, as the rheological response of these materials is dependent on the shear history of the sample.

**A.2.3 Non-Newtonian Fluids: Viscoelastic Behaviour**

*Viscoelastic* materials exhibit the combined characteristics of both a solid and a liquid. A purely elastic solid stores energy and deforms reversibly; the strain is proportional to the stress and when the stress is released, the solid recovers its original volume and shape. Liquids do not store energy when stressed; the viscous response is to dissipate the energy as heat as the fluid flows. In a viscoelastic material, a combination of elastic and viscous (damping) responses is observed and the stress gradually dissipates.

Steady shear viscosity measurements can be obtained for all fluids. However, in order to obtain viscoelastic parameters, non-steady state deformations are often used. These dynamic testing techniques are either transient (e.g. tests of start-up flow, cessation of steady shear flow) or oscillatory (e.g. when a sinusoidal stress is applied).

Whether a viscoelastic material behaves more as a viscous liquid or elastic solid depends on the Deborah number (i.e the ratio of the time scale of the experiment and the time required for the system to respond to the stress or deformation). High Deborah numbers correspond to materials exhibiting solid-like behaviour; low Deborah numbers correspond to materials exhibiting liquid-like behaviour.
Appendix B

A BRIEF OVERVIEW OF CAPILLARY RHEOMETRY THEORY

The design of the Multi-Pass Rheometer (MPR) is based on a capillary rheometer. In the MPR, when a sample is passed through the capillary section at a given piston speed, \(v_p\), a pressure difference, \(\Delta P\), is obtained as a function of time.

For a capillary of length \(L\) and internal diameter \(D\), the wall shear stress \(\tau_w\) in steady flow is independent of the rheological properties of the fluid. A force balance in the axial direction gives:

\[
\tau_w = \frac{D\Delta P}{4L}
\]  

(B.1)

where \(\Delta P\) is the pressure difference across the capillary.

The \(\Delta P/L\) ratio in Equation B.1 may need to be adjusted if entrance and exit effects are significant. These arise when fluid flow in the entry regions of the capillary causes: (1) viscous and inertial losses and (2) the redistribution of entrance velocities within the capillary. Use of a long capillary (\(L/D > 10\)) can help to minimise the need for corrections (Pierce and Schoff, 1982). Otherwise, ‘Bagley plots’ can be used to adjust the \(\Delta P/L\) ratio; this requires \(\Delta P\) measurements to be made with several capillaries of fixed diameter but with varying length, at a particular volumetric flow rate \(Q\).

For a Newtonian fluid in steady laminar flow with no slip at the wall, the wall shear rate \(\dot{\gamma}_w\) can be expressed as:

\[
\dot{\gamma}_w = \frac{32Q}{\pi D^3} = \frac{8\nu_p D_b^2}{D^3}
\]  

(B.2)

where \(D_b\) is the internal diameter of the rheometer barrel in the MPR (\(D_b \geq D\)).
From Equations B.1 and B.2, the viscosity $\eta$ of the fluid can be obtained:

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} \quad (B.3)$$

For *time-independent non-Newtonian fluids*, the Rabinowitsch-Mooney equation is used instead of Equation B.2 to calculate the wall shear rate, where $R$ is the internal radius of the capillary. This is given by:

$$\dot{\gamma}_w = f(\tau_w) = \left( \frac{3Q}{\pi R^3} \right) + \left( \tau_w \right) \left[ \frac{d Q/(\pi R^3)}{d \tau_w} \right] \quad (B.4)$$

For *time-dependent non-Newtonian fluids*, such as high-active LAS, the shear stress and apparent viscosity change over time with the application of a steady shear rate. Therefore, traditional flow curves, graphs of shear stress plotted against shear rate, are not the most appropriate way to represent the rheological behaviour of fluids that are highly time dependent.

One means of observing the rheological behaviour of a time-dependent fluid is by applying a steady shear rate and measuring its shear stress response over time. This is the approach that has been taken in this study of high-active LAS. From experiments in the MPR, $\Delta P$ and $\Delta P_p$ values were obtained from pseudo-steady shear; these parameters are related to the shear stress (Equation B.1). Where appropriate, Equation B.2 has been used to convert the MPR piston velocity $v_b$ to an ‘apparent’ wall shear rate, following McKeown (2001) and McKeown *et al.* (2003). This apparent wall shear rate is not the true wall shear rate, however it provides a useful approximation to it. As the time-dependency of high-active LAS means that only approximate wall shear rates can be obtained with Equations B.2 and B.4, Equation B.2 is used in preference to Equation B.4 as it does not require as many experiments to be performed in order for the equation to be used.
Appendix C

A BRIEF OVERVIEW OF X-RAY SCATTERING

The purpose of Appendix C is to provide a brief description of the basic theory behind X-ray diffraction and some of the useful information that can be gained from using this measuring technique. There are a number of books written on this subject. For a more comprehensive treatment of X-ray diffraction, the reader is referred to the texts used in this appendix: Guinier (1963), Kakudo and Kasai (1972), Vickers (1995), and Cullity and Stock (2001).

C.1 X-ray Scattering Theory

When a monochromatic beam of X-rays strikes an atom, several effects can occur: the incident X-rays are absorbed and also scattered. Both coherent and incoherent scattering occur simultaneously and in all directions. With coherent scattering, the tightly bound electrons within the atom cause the scattering of X-rays with the same wavelength as the incident beam. Incoherent scattering occurs with more loosely bound electrons where the scattered X-rays are of a slightly increased wavelength when compared to the incident beam.

Although it is the interaction with the electrons that causes scattering, the atomic centres are commonly treated as scattering centres. If the atom is part of a large group of atoms arranged in space in a regular periodic fashion, such as a crystalline or liquid crystalline material, diffraction of the coherently scattered X-rays occurs. Diffracted X-ray beams are the result of reinforced coherent scattering in certain directions (Bragg’s Law) and cancellation in all other directions. In wide-angle X-ray diffraction experiments, analysis of the peak intensity, peak position and peak profile from the diffraction pattern can yield valuable information about the microstructure of the sample.
A monochromatic X-ray beam can be treated as an electromagnetic wave with a defined amplitude, phase, direction and constant wavelength $\lambda$. Figure C.1 shows the coherent scattering of incident X-rays by two electrons at points O and P, where the unit vectors $S_o$ and $S$ denote the incident and scattered beams respectively.

![Figure C.1](image-url)

**Figure C.1.** Schematic diagram of: (a) the phase difference between X-rays scattered by two electrons at O and P; (b) the definition of the scattering vector $s = (S - S_o)/\lambda$. After Vickers (1995).

The path difference $\delta$ between the waves scattered at point O and point P is given by:

$$\delta = OR - QP = S \cdot r - S_o \cdot r = (S - S_o) \cdot r \quad (C.1)$$

The corresponding phase difference $\phi$ is given by:

$$\phi = \frac{2\pi \delta}{\lambda} = \frac{2\pi (S - S_o) \cdot r}{\lambda} = 2\pi s \cdot r \quad (C.2)$$

The scattering vector $s$ is defined in Figure C.1 (b) as $s = (S - S_o)/\lambda$, where the dimensions of $s$ are $[L]^{-1}$. The length of $s$ is given by:

$$s = \frac{2\sin \theta}{\lambda} \quad (C.3)$$

For a sample of N scattering centres, the *structure factor* $F(s)$ is the summation of the waves contributed to by all the scattering centres within the total irradiated volume $V$: 
\[ F(s) = \sum_{j=1}^{N} f_j \exp[(2\pi i)s \cdot r_j] \quad (C.4) \]

F(s) is a complex number and expresses both the amplitude and phase of the resultant wave. The atomic scattering factor \( f \) gives the efficiency of scattering from a given atom in a given direction; it is defined as a ratio of amplitudes from the wave scattered by an atom to the wave scattered by one electron.

Replacing the discrete points in positions \( r_j \) with a continuous function for electron density \( \rho(r) \), and integrating over \( V \) gives:

\[ F(s) = \int \rho(r) \exp[(2\pi i)s \cdot r] \, dV_r = \text{FT}[\rho(r)] \quad (C.5) \]

### C.1.1 Diffraction Peak Intensity

As discussed in the section above, the scattered intensity obtained during X-ray diffraction experiments is a function of the electron density of the irradiated sample. However, the absorption of X-rays can also affect the peak intensity as described in the following equation:

\[ I_s = I_o \exp(-\mu x) \quad (C.6) \]

where \( I_o = \) intensity of incident X-ray beam and \( I_s = \) intensity of transmitted beam after passing through a sample of thickness \( x \). The linear absorption coefficient \( \mu \) is proportional to the sample density.

### C.1.2 Diffraction Peak Position

Information on the structure of a crystalline or liquid crystalline solid can be obtained from Bragg’s Law:

\[ n \lambda = 2d \sin \theta \quad (C.7) \]

where \( d \) is the inter-planar spacing (d-spacing) and \( n \) is an integer representing the diffraction order. This equation states the essential condition that must be met if diffraction is to occur and relates the scattering angle \( 2\theta \) to the fundamental repeat distances in the sample.
In Figure C.2, an illustration of Bragg’s Law is given for a lamellar liquid crystalline material with one-dimensional periodicity. A beam of incident X-rays impinges on two scattering centres lying on two successive crystal planes. The path difference between the X-rays interacting with the scattering centres on the top and bottom crystal planes is given by \( AB + BC \). Constructive interference (i.e. diffraction) only occurs when the path difference is equal to the wavelength \( \lambda \) (or an integer multiple of \( \lambda \)).

From Bragg’s Law, it is evident that larger the characteristic scattering angle, the smaller the microstructural repeating distance.

### C.2 X-ray Data from a Two-Dimensional Detector

There are various diffractometers and detectors that can be used for X-ray scattering experiments. Two-dimensional area detectors, such as the one used in this work (Chapter 3, Figure 3.2), provide X-ray scattering data not only of the fundamental repeat distance or d-spacing within the sample, but also the specific types of structures that are present. From an area detector, the sharpness and azimuthal (\( \chi \)) angular distribution of the detected X-ray intensities reflect the regularity in the variation of electron density along different directions in the sample. X-ray scattering experiments with area detectors are particularly useful for liquid crystalline systems.
Figure C.3 (based on Kakudo and Kasai, 1972 and Cullity and Stock, 2001) is a summary of different microstructures that can form based on stacked lamellae and the corresponding two-dimensional X-ray scattering pattern that would be observed.

**Figure C.3.** Schematic of long-range ordered structures shown to the right of each column; to the left of each column, the corresponding two-dimensional X-ray scattering patterns are shown where the central black dot marks the beam-stop position and the detected X-rays are represented by the orange markings. Images labelled (a) to (f) correspond to planar lamellae orientated in a particular direction as shown. The images shown in (g) correspond to microstructures where there are statistically symmetrical assemblies of lamellae: e.g. (i) spherulites, (ii) MLVs, (iii) unorientated planar lamellae (After Kakudo and Kasai, 1972 and Cullity and Stock, 2001).
Appendix D

Calculation of the Effective Ion Size for Salts Used in Experiments

In this section, calculations to estimate the effective size of the various ions added to high-active LAS during experiments are presented. These results are discussed in Chapter 5. The data used for calculations were obtained from Alberty and Silbey (1997) and shown in Tables D.1 and D.2.

For ions consisting of only one species, the effective ion size (diameter) is simply twice the ionic radius (Table D.1). For ions involving covalent bonds, a characteristic length across the ion was selected and the contributions from the atoms in the selected part of the ion were added together using the covalent radii (Table D.2).

Table D.1. Ion radii data obtained from crystal structure data.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic radius (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>95</td>
</tr>
<tr>
<td>K⁺</td>
<td>133</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>181</td>
</tr>
</tbody>
</table>
Table D.2. Covalent radii for atoms

<table>
<thead>
<tr>
<th>Bond radii</th>
<th>Radius (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td></td>
</tr>
<tr>
<td>Single-bond radius</td>
<td>30</td>
</tr>
<tr>
<td>C</td>
<td></td>
</tr>
<tr>
<td>Single-bond radius</td>
<td>78</td>
</tr>
<tr>
<td>Double-bond radius</td>
<td>67</td>
</tr>
<tr>
<td>N</td>
<td></td>
</tr>
<tr>
<td>Single-bond radius</td>
<td>70</td>
</tr>
<tr>
<td>O</td>
<td></td>
</tr>
<tr>
<td>Single-bond radius</td>
<td>66</td>
</tr>
<tr>
<td>Double-bond radius</td>
<td>56</td>
</tr>
<tr>
<td>Si</td>
<td></td>
</tr>
<tr>
<td>Single-bond radius</td>
<td>117</td>
</tr>
<tr>
<td>P</td>
<td></td>
</tr>
<tr>
<td>Single-bond radius</td>
<td>110</td>
</tr>
<tr>
<td>Double-bond radius</td>
<td>100</td>
</tr>
<tr>
<td>S</td>
<td></td>
</tr>
<tr>
<td>Single-bond radius</td>
<td>104</td>
</tr>
</tbody>
</table>

D.1 Calculations

The calculations shown in this section are for ions consisting of covalent bonds. The schematic ionic structures that are shown are not meant to be indicative of the actual bond angles; they are provided to give an indication of the connectivity between atoms and types of covalent bonds existing within the ions. At the end of this chapter a summary is given for all the ions added during experiments (Table D.3).
D.1.1 Ammonium ion

*Formula:* NH$_4^+$ (tetrahedral, bond angle *ca.* 109.5°)

*Characteristic length:* One side of the tetrahedron (i.e. the length is estimated from the distance between the centres of 2 hydrogen atoms added to the 2 hydrogen radii at the ends).

*Calculation:*

\[
[2(70+30) \times \sin(54.8°)] + 2(30) = 223 \text{ pm}
\]

D.1.2 Citrate ion

*Formula:* C$_6$H$_5$O$_7$$^{3-}$

*Schematic structure:*

\[\text{Characteristic length 1: As shown in the schematic above. This is the distance between the tetrahedral side (centre of C atom to the O atom plus the hydrogen atom) added to the distance between trigonal C to adjoining O atom, plus the remaining radii at the ends.}\]

*Calculation:*

\[
[2(156) \times \sin(54.8°)] + 2(66) + 2(30) + [(156)^2 + (144)^2 - 2(156)(144) \times \cos(120°)]^{0.5}
\]

\[= 255 + 132 + 120 + 259.9\]

\[= 707 \text{ pm}\]
Characteristic length 2: As shown in the schematic above. This is the distance between the centre of the C' atoms added to the distance between the centre of the C' and O′ atoms plus the remaining O′ radii at the ends.

Calculation:

\[ [2(156) \times \sin(54.8^\circ)] + 2\left[\left((156)^2 + (144)^2 - 2(156)(144) \times \cos(120^\circ)\right)^{0.5}\right] + 2(61) \]

\[ = 255 + 2(259.9) + 122 \]

\[ = 897 \text{ pm} \]

D.1.3 Disilicate ion

Schematic structure of typical ionic species:

![Schematic structure of disilicate ion]

The Si atoms have bond angles of ca. 109.5° (tetrahedral).

Characteristic length 1: As shown in the schematic above. This is the distance between the centres of the tetrahedral O′ atoms plus the remaining O′ radii and H atoms at the ends.

Calculation:

\[ [2(183) \times \sin(54.8^\circ)] + 2(66) + 4(30) \]

\[ = 299 + 132 + 120 \]

\[ = 551 \text{ pm} \]
Characteristic length 2: As shown in the schematic above. This is the distance between the centre of the terminal O\textsuperscript{-} atoms plus the remaining O\textsuperscript{-} radii at the ends.

Calculation:

\[ 2[2(183) \times \sin(54.8^\circ)] + 2(66) \]
\[ = 2(299) + 132 \]
\[ = 730 \text{ pm} \]

D.1.4 Nitrate ion

Formula: NO\textsubscript{3}\textsuperscript{−} (trigonal planar, bond angle ca. 120\(^\circ\))

Characteristic length: One side of the triangle (i.e. the length is estimated from the distance between the centres of 2 oxygen atoms added to the 2 oxygen radii at the ends).

Calculation:

\[ [2(70+59) \times \sin(60^\circ)] + 2(59) = 341 \text{ pm} \]

D.1.5 Phosphate (tribasic) ion

Formula: PO\textsubscript{4}\textsuperscript{3−} (tetrahedral, bond angle ca. 109.5\(^\circ\))

Characteristic length: One side of the tetrahedron (i.e. the length is estimated from the distance between the centres of 2 oxygen atoms added to the 2 oxygen radii at the ends).

Calculation:

\[ [2(168.5) \times \sin(54.8^\circ)] + 2(61) = 397 \text{ pm} \]
D.1.6 Phosphate (monobasic) ion

*Formula:* PO$_2$ (OH)$_2^-$ (tetrahedral, bond angle *ca.* 109.5°)

*Characteristic length:* One side of the tetrahedron (i.e. the length is estimated from the characteristic length calculated for the phosphate tribasic ion added to a hydrogen atom).

*Calculation:*

\[2(168.5) \times \sin(54.8°) + 2(61) + 2(30) = 457 \text{ pm}\]

D.1.7 Sulfate ion

*Formula:* SO$_4^{2-}$ (tetrahedral, bond angle *ca.* 109.5°)

*Characteristic length:* One side of the tetrahedron (i.e. the length is estimated from the distance between the centres of 2 oxygen atoms added to the 2 oxygen radii at the ends).

*Calculation:*

\[2(170) \times \sin(54.8°) + 2(66) = 410 \text{ pm}\]

D.1.8 Tetramethyl-ammonium ion

*Formula:* N(CH$_3$)$_4^+$ (tetrahedral, bond angle *ca.* 109.5°)

*Characteristic length:* One side of the tetrahedron (i.e. the length is estimated from the distance between the centres of 2 carbon atoms added to twice the distance between the centre of a carbon atom to an adjoining hydrogen atom plus the hydrogen radii at the ends).

*Calculation:*

\[2(148) \times \sin(54.8°) + 2[2(108) \times \sin(54.8°)] + 2(30) = 656 \text{ pm}\]
D.1.9 Water molecule

Formula: \( \text{H}_2\text{O} \) (bond angle \textit{ca.} 105°)

Schematic structure:

![Schematic structure of water molecule]

Characteristic length: As shown above. This is the distance between the centres of 2 hydrogen atoms plus the remaining hydrogen radii at the ends).

Calculation:

\[ [2(96) \times \sin(52.5°)] = 152 \text{ pm} \]

---

Table D.3. Summary of estimated ion/molecule sizes (shown in ascending order). Where an additional alternative effective size was calculated, this is shown in brackets.

<table>
<thead>
<tr>
<th>Ion/molecule</th>
<th>Effective size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (\text{H}_2\text{O})</td>
<td>1.5</td>
</tr>
<tr>
<td>Sodium (\text{Na}^+)</td>
<td>1.9</td>
</tr>
<tr>
<td>Ammonium (\text{NH}_4^+)</td>
<td>2.2</td>
</tr>
<tr>
<td>Potassium (\text{K}^+)</td>
<td>2.7</td>
</tr>
<tr>
<td>Nitrate (\text{NO}_3^-)</td>
<td>3.4</td>
</tr>
<tr>
<td>Chloride (\text{Cl}^-)</td>
<td>3.6</td>
</tr>
<tr>
<td>Phosphate, tribasic (\text{PO}_4^{3-})</td>
<td>4.0</td>
</tr>
<tr>
<td>Sulfate (\text{SO}_4^{2-})</td>
<td>4.1</td>
</tr>
<tr>
<td>Disilicate (\text{SiO(OH)O}_2)</td>
<td>5.5 (7.3)</td>
</tr>
<tr>
<td>Phosphate, monobasic (\text{PO}_2 (\text{OH})_2)^{\text{2-}}</td>
<td>4.6</td>
</tr>
<tr>
<td>Tetramethyl-ammonium (\text{N(CH}_3)_4)^{\text{+}}</td>
<td>6.6</td>
</tr>
<tr>
<td>Citrate (\text{C}_6\text{H}_5\text{O}_7)^{\text{3-}}</td>
<td>7.1 (9.0)</td>
</tr>
</tbody>
</table>

---
Appendix E

Calculation of Apparent Wall Shear Rates During Industrial Paste-Structuring

In this section, calculations to determine typical apparent wall shear rates in the industrial paste-structuring process are given.

In the industrial process, high-active LAS is passed through a twin-screw extruder and exits through a die plate with an orifice of typically 10 mm diameter. The paste is fed into the extruder at a rate of *ca.* 5,000 kg h⁻¹ and the typical residence time is between 45-120 seconds. The high-active LAS enters the extruder at 60 °C, although it is usually cooled as it passes along the barrel of the extruder.

Although high-active LAS also undergoes shearing in the barrels of the twin-screw extruder, we will only consider the apparent wall shear rate that is applied as the paste exits the extruder through the die.

Assuming a paste density of 1000 kg m⁻³, this gives a volumetric flowrate Q (m² s⁻¹) as follows:

\[
Q = \frac{\text{mass flow rate (kg s}^{-1})}{\text{density (kg m}^{-3})} = \frac{5000 \div 3600}{1000} = 1.4 \times 10^{-3} \text{ m}^3 \text{ s}^{-1}
\]

Assuming there is no slip at the wall, the apparent wall shear rate \(\dot{\gamma}_w\) (s⁻¹) can be approximated by Equation B.2:

\[
\dot{\gamma}_w = \frac{32Q}{\pi D^3} = \frac{32 \times 1.4 \times 10^{-3}}{\pi \times (0.01)^3} = 14,000 \text{ s}^{-1}
\]
where $D$ (m) is the diameter of orifice at the end of the extruder.

Thus, high-active LAS is subject to typical apparent wall shear rates of $ca. 14,000 \text{s}^{-1}$ during industrial paste-structuring. This is much higher than the typical apparent wall shear rate of $10 \text{s}^{-1}$ that high-active LAS experiences as it is pumped through pipes for transportation purposes (McKeown, 2001).

The residence time of high-active LAS on the industrial twin-screw extruder is typically only 45-120 seconds. During the course of this work, shearing experiments have been carried in the MPR at an apparent wall shear rate of $1,100 \text{s}^{-1}$ for typically an hour. The time-dependent nature of MLV formation in high-active LAS during the paste-structuring process means that it is likely that both the shear rate and duration of shear contribute to the level of paste structuring or the paste firmness achieved.
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