Multilamellar Vesicles in a Commercial Surfactant System

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The manufacture of concentrated detergent granules in the detergent industry can be achieved by the incorporation of surfactant pastes, such as linear alkylbenzene sulfonate paste (LAS)—a lamellar liquid crystalline material (surfactant concentration of ca. 78 wt. %). LAS paste was processed at 25°C and 60°C, in both the absence and presence of sodium disilicate ($Na_2O{:}2SiO_2$) additive, and the effect on the formation of shear-induced multilamellar vesicle (MLV) microstructures was studied. Our results suggest that LAS pastes of high hardness and stiffness are always associated with MLV microstructures and vice versa—these are known as "structured" pastes in industry, and also appear nonadhesive. MLVs are able to form from "pure" LAS at 25°C, although, at 60°C, sodium disilicate is necessary. With increased processing time, the size of the MLVs decreases and becomes more uniform—pastes are also increasingly hard and stiff. When stored, "structured" pastes eventually revert back to being soft and sticky, reflecting the metastable nature of the MLVs.

Introduction

Linear alkylbenzene sulfonate (LAS) is the most-used surfactant in household detergents (Matheson, 1996), but despite its commercial importance, published information is limited. (The acronym LAS used in this article refers to what is commonly known in industry as "high-active" LAS paste (a paste-like fluid of ca. 78 wt. % surfactant, in the form of linear alkylbenzene sulfonate salts, the remainder comprising of mostly water.) LAS, as used industrially for the production of compact detergent powders, is a highly concentrated surfactant mixture, which provides the cleaning action of the detergent. The "active matter" of LAS consists of anionic surfactant molecules (these take the form of various isomers of linear alkylbenzene sulfonate sodium salts), while the rest of the paste consists of water and various impurities. Industrial surfactants used in the agglomeration process for compact detergent production are typically around 80 wt. % active matter; at this high surfactant concentration, LAS is a lyotropic liquid crystalline material of lamellar bilayer structures (McKeown, 2001).

Compact detergent powders produced by methods of agglomeration use the LAS paste as a binder to hold together various builders, bleaches, and fillers to form the finished detergent granules. In order for high-active LAS paste to be suitable for the agglomeration process, processing of the paste itself is necessary to modify its properties from its initial state—it must be adhesive enough to act as a "glue" for the particulate material, but also not so sticky as to inhibit the formation of separate granules. At temperatures of approximately 70°C, the paste appears soft, yellow, and adhesive. In this state, it is transportable, as it can be pumped through pipes in the factory. By processing the heated paste with additives in an extruder, where paste is subjected to high shear rates, the properties of the paste are modified such that the paste appears firm, white, and nonadhesive. Industrialists term paste with such properties as being "structured," and any process to achieve this effect as "paste-structuring" (Aouad et al., 1997, 2000). These modified properties enable high-active LAS paste to be used in agglomeration.

From an industrial perspective, it is desirable to be able to predict paste properties (such as stickiness and hardness)

Correspondence concerning this article should be addressed to M. S. Liaw based on the processing history of the paste. From a scientific viewpoint, the change in LAS paste properties during "structuring" is interesting as it is associated with a change in the microstructure of the material.

In the literature, surfactant systems, where shear-induced changes in microstructure are studied, tend to form lamellar phases at relatively high concentrations of surfactant (typically ca. ~20–60 wt. %), and are capable of remaining stable for very dilute systems (<10 wt. %) (Diat and Roux, 1993). Mortensen (2001) gives a brief overview of work in this field, mentioning both theoretical and experimental studies.

Theoretical studies have been carried out investigating the undulation instability of lamellar phases. Helfrich (1994) describes three classes of bilayer phases (connected, planar, and vesicular) in terms of a simple model based on membrane bending elasticity. However, in this model for a dilute system, any interaction between bilayers is neglected, as it is assumed that the fluid bilayers are driven apart by their thermal undulations and van der Waals attraction and electrostatic repulsion forces are not accounted for. Auernhammer et al. (2000) have devised a hydrodynamic description of smectic A liquid crystals showing the origin of the undulation instability under shear flow, while Zilman and Granek (1999) have proposed a mechanism for MLV or "onion" formation based on this instability, where a critical shear rate for onion formation is predicted.

Experimental investigations on shear-induced planar lamellar to MLV transitions have been carried out on a variety of dilute surfactant systems. Diat et al. (1993) developed an "orientation rheogram" for an anionic surfactant in a quaternary system describing the subsequent "out-of-equilibrium" steady-state structures formed during the application of shear on lyotropic lamellar phases; various shear rates and bilayer volume fractions (dilutions) were examined. They found three different states of orientation present, and defined dynamic transitional boundaries between the orientation states. At very low shear rates, they found that the lamellar phase orientated itself so as to have its layers in the shear plane, and that defects were present. At medium shear rates, MLVs were formed, while, and at very high shear rates, an orientated state was again formed, but this time without defects. It was also found that the diameter of MLVs was fixed by a balance between viscous and elastic stresses and varied as the inverse square root of the shear rate. Some other interesting observations from the study were that steady state was reached more quickly at higher shear rates, and that the critical value of the shear rate for MLV formation appeared to decrease when the bilayer spacing increased (that is, with increased dilution).

Similar behavior to the system used by Roux et al. has been observed by Le et al. (2000, 2001) in a simpler nonionic surfactant system, although a continuous "sponge-phase" was observed, as well as a biphasic planar lamellar/MLV state; temperature was seen to have a critical effect. Schmidt et al. (1998, 1999) and Zipfel et al. (1999) studied the effect of shear on polymeric surfactant systems. In these systems shear-thickening occurred at low polymer concentrations (due to MLV formation from planar bilayers); however, at high polymer concentrations, a decrease in viscosity with shear was observed, due to the orientation of planar lamellae.

There have been some studies on the influence of charge density on lamellar systems. Bergmeier et al. (1999) investigated the aqueous system TDMAO/TTABr/*n*-hexanol [TDMAO—tetradecyldimethylamineoxide and TTABr—tetradecyltrimethylammonium bromide] and found that, at low TTABr content, preferentially planar lamellae are formed, while MLVs appear at higher TTABr content. Shearing the system transforms the planar lamellae to MLVs—an increase of the shear rate causes vesicle shells to be stripped off, and, at high shear rates, unilamellar vesicles are formed. Léon et al. (2000) studied flow-structure properties and the relation between salinity and defect structures in a dilute AOT/water/NaCl system [sodium bis(2-ethylhexyl) sulfosuccinate (AOT) surfactant concentration of 7 wt. %]. 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" 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 would occur after a certain delay time and that the delay would increase with salinity.

Lukaschek et al. (1996) used rheo-NMR techniques to study the lamellar phases of concentrated aqueous ethylene oxide surfactants (35, 60, and 80 wt. %) and the evolution of shear-induced structures and the dependence on surfactant concentration, shear geometry, and shear history. Among their conclusions is that the stability of MLV structures is dependent on concentration.

While the literature provides an interesting background for this study of an industrial material, no previous work has involved commercial detergent systems of the high surfactant concentration used in industry, nor looked at the types of additives used to achieve "paste structuring" for the detergents. In this article we describe how temperature, shear, and additives interact to determine the physical properties and microstructure of one of the world's most widely used surfactant.

Methods and Materials

LAS samples were obtained from the Procter and Gamble Newcastle Technical Centre, U.K. The chemical composition of a typical "high-active" LAS batch is given in Table 1. In the experiments that are described in this article, the "active matter" of the LAS paste is 78 wt. %.

Amorphous sodium disilicate powder ("Pyramid P70" from INEOS Silicas Ltd., Netherlands; with molar ratio $Na_2O{:}2SiO_2$) was used as the additive, with powder particles between 65 μm and 250 μm in diameter.

The experiments described in this article were carried out using the Cambridge Multi-Pass Rheometer (MPR) (Mackley et al., 1995; McKeown et al., 2003). The MPR (Figure 1a) is a double-piston capillary rheometer, consisting of three sections, in which the sample is fully enclosed and pressurized. The MPR allows high apparent wall shear rates to be investigated (typically 10^5 s^{-1}), with control and measurement of pressure, temperature, and flow made possible. An X-ray unit can be attached to the MPR to allow X-ray measurements to be taken during an experiment (Figure 1b).

In order to process the LAS paste, the MPR was used in "multipass" mode, in which the sample is forced through a test section repeatedly. The piston motion is as follows: (1)

Table 1. Typical Composition of LAS Paste Obtained from Procter & Gamble*

Composition	Wt. %
Analytical Data	
Active Matter	77.2
H_2O (Water)	19.10
LAB (Linear alkylbenzene)	1.65
Na_2SO_4 (Sodium sulfate)	0.42
NaOH (Sodium hydroxide)	0.37
NaCl (Sodium chloride)	0.16
Alkyl Chain Distribution Data	
< Linear C_{10}	0.5
Linear C_{10}	10.9
Linear C_{11}	31.3
Linear C_{12}	31.0
Linear C_{13}	19.8
Linear C_{14}	0.5
> C_{14}	0.0
Tetralins and complex hydrocarbons including branched material	6.0
Total	100.0
of which 2-phenyl isomer content	18.4

*Newcastle Technical Centre, England; after McKeown (2001).

pistons are moved together in the same direction at a constant velocity for a set distance or "amplitude"; (2) pistons are then held in position for a period ("idle time"); (3) the steps above are repeated with the direction of piston movement reversed after each period of idle time.

Pressure transducers placed on either side of the test section enable the instantaneous pressure difference across the test section ΔP to be calculated. During one cycle of piston movement, the ΔP plateau value is referred to as the pseudo-steady-state value ΔP_p. This value corresponds to the extrusion pressure of the sample as it passes through the MPR test section, and is a measure of the viscosity-related "resistance to flow" or stiffness demonstrated by the sample. LAS often exhibits time-dependent viscous behavior (rheopexy and thixotropy) during continuous steady shear. Thus, ΔP_p, although remaining constant during a single piston cycle, is likely to change gradually over many cycles, until the material reaches steady state. Due to the time-dependent structural changes occurring with LAS, calculations of true shear rate and viscosities using Rabinowitsch-Mooney corrections (Holland and Bragg, 1995) were not possible.

The MPR test section used for these experiments was a capillary assembly designed to minimize the contribution of "end effects" at the entrances of the capillary to the total pressure difference during shear. The dimensions of the capillary itself were 2 mm internal dia. and 90 mm total length. To enable X-ray measurements, the central portion of the capillary contained a carbon-fiber insert. Usually, a Bagley correction (Bagley, 1956) is applied in capillary rheometry to correct for entrance effects; however, the time-dependent nature of the shear-induced structures in LAS did not allow for this.

The X-ray unit (Bruker AXS, Madison, WI) attached to the MPR was operated in transmission mode; the X-ray beam path through the MPR capillary is shown in Figure 1b. A Siemens Kristalloflex 760 X-ray generator, equipped with a graphite monochromator, and a collimator of 0.8 mm dia., was used. For all experiments, the voltage and current were kept at 45 kV and 45 mA. The transmitted and scattered X-rays were collected with a Siemens HI-STAR detector (active area of 115 mm diameter). All the X-ray data were collected using an exposure time of 200 s. In order to reduce the "noise" due to background scatter, a helium-filled tube was placed in the path between the sample and detector (the sample-detector distance was kept at approximately 76.3 cm). Calibration of the sample-detector distance was carried out using silver behenate ($C_{22}H_{43}O_2Ag$) (Eastman Kodak, Rochester, NY).

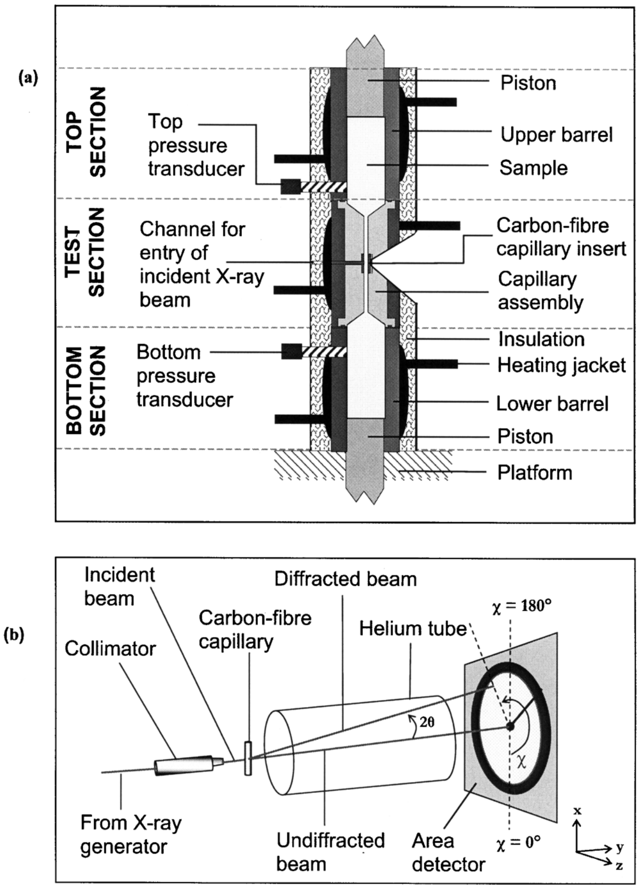


Figure 1. Multi-Pass Rheometer (MPR) and X-ray facility.

(a) MPR setup showing barrels and capillary assembly; (b) X-ray unit showing beam direction in relation to MPR capillary, where 2θ is the scattering angle and χ is the azimuthal angle; after McKeown et al. (2003).

LAS paste was stored in a sealed container at ca. 18°C prior to experiments. Approximately 17 g of sample was loaded into the MPR, and then left for at least 45 min to equilibriate to the experimental temperature of either 25°C or 60°C. Prior to loading, the sodium disilicate powder was mixed through the LAS paste with a spatula—in the absence of additives the LAS was "mixed" with the spatula for consistency in loading procedure. For all experiments, a vacuum pump removed air from the system and the pistons were used to compress the sample to a static pressure of 4 bar before shearing of the sample commenced. The piston speed used during multipass mode was 5.1 mm s^{-1} (corresponding to an

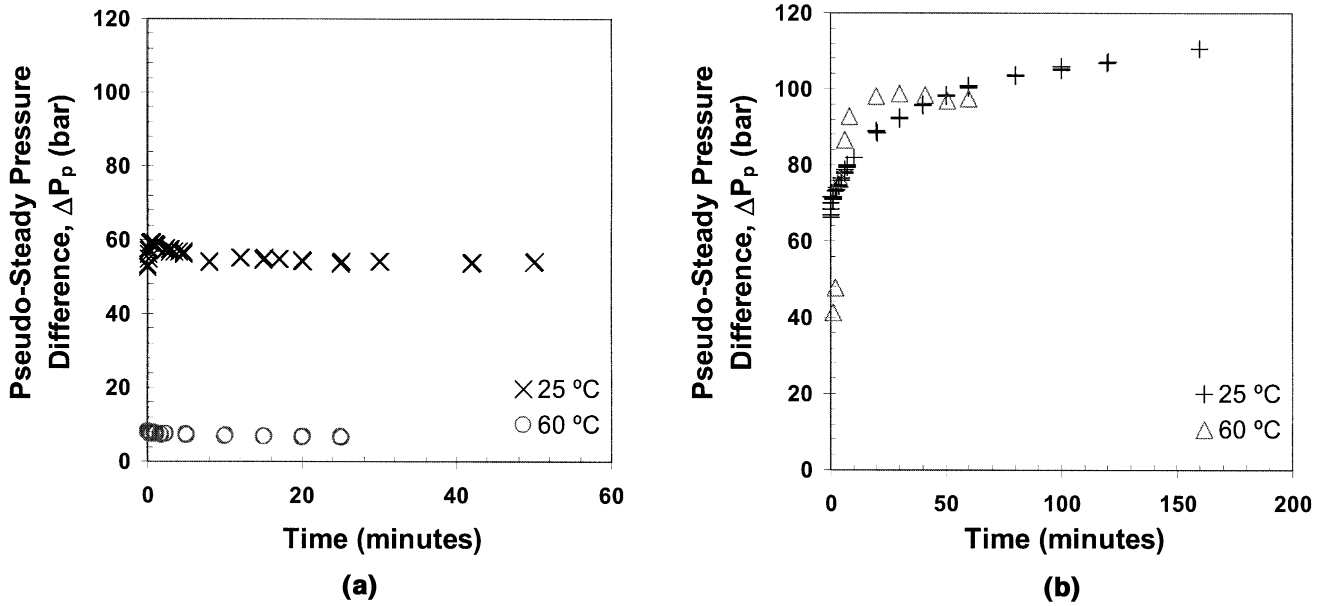


Figure 2. Pseudo-steady pressure difference vs. time data obtained from the MPR using multipass shear.

(a) LAS alone, processed at 25°C and 60°C; (b) LAS with 10 wt. % sodium disilicate, processed at 25°C and 60°C.

apparent shear rate of 1,100 s^{-1}), while the amplitude was 3 mm with 0.02 s idle time.

After shearing, extrudate samples from the MPR capillary assembly were stored in sealed vials at ca. 18°C, for between one and eight days, prior to scanning electron microscopy (SEM) observations. A Philips XL30 FEG (Fei Company, OR) scanning electron microscope was used. Portions of the extrudate were frozen for cryogenic SEM by quench cooling in sub-cooled "slushy" nitrogen (−210°C) to limit the size of ice crystals formed. The frozen samples were fractured to expose the circular cross-section of the extrudate and then the surface was thinly coated with a gold alloy. During observations, the SEM sample stage was kept at ca. −150°C.

Results and Discussion

Effect of temperature during processing in the MPR

LAS paste was processed to a rheological steady state at two different process temperatures (25°C and 60°C) in the absence of sodium disilicate additive. Figure 2a shows the pseudo-steady differential pressure data typically observed as a function of processing time.

At 25°C, before steady state is reached (that is, the pseudo-steady differential pressure measurement is not yet at a constant value), the material exhibits slight rheopectic (viscosity increases with time at a given shear rate) and then thixotropic (viscosity decreases with time at a given shear rate) behavior. However, rheopectic behavior at 60°C is not observed prior to steady state. At steady state, the differential pressure values reached for LAS processed at 25°C are much higher (ca. 54 bar) than LAS processed at 60°C (ca. 7 bar), indicating that the processed paste at 25°C is more resistant to flow than the processed paste at 60°C. The paste processed at 25°C also appears qualitatively much harder and stiffer ("structured").

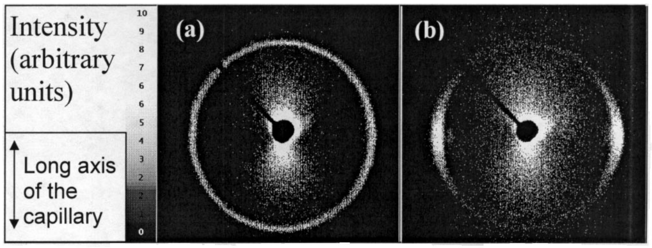


Figure 3. X-ray diffraction patterns of LAS alone collected during shearing to steady state in the MPR.

Process temperatures: (a) 25°C (after 30 min shear); (b) 60°C (after 20 min shear).

The X-ray diffraction patterns of LAS during processing to steady state at 25°C and 60°C (Figure 3) show diffraction rings corresponding to the characteristic (bilayer) repeat distance of 30 Å. However, there is a difference in the distribution of scattering intensity over values of the azimuthal angle χ as shown in Figure 4. At 60°C, it is clear that over the "equator" (that is, $\chi = 90°$ and 270°), there is a far greater scattering intensity than at other values of χ. At 25°C, however, the scattering intensity is more evenly distributed around values of χ. This is consistent with results obtained by McKeown (2001) and with co-workers (McKeown et al., 2003); the evenly distributed scattering observed during processing at 25°C was attributed to the formation of MLVs, while the intense scattering at the equator at 60°C was due to the orientation of planar lamellae. The slight increase in intensity at the equator for processing at 25°C is likely to be caused by the presence of orientated planar lamellae not yet transformed into MLVs, as will be seen in Figures 9a and 9b.

In the center of the capillary, planar lamellae will orient parallel to the flow, but randomly in the plane perpendicular to this; some oriented lamellae will, therefore, scatter equa-

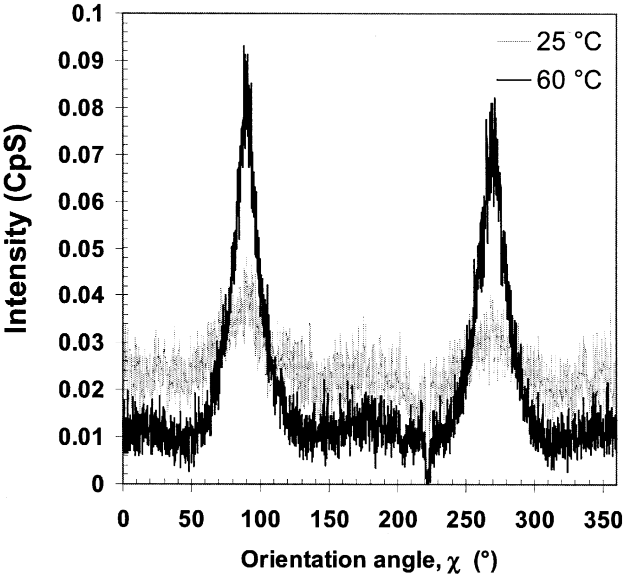
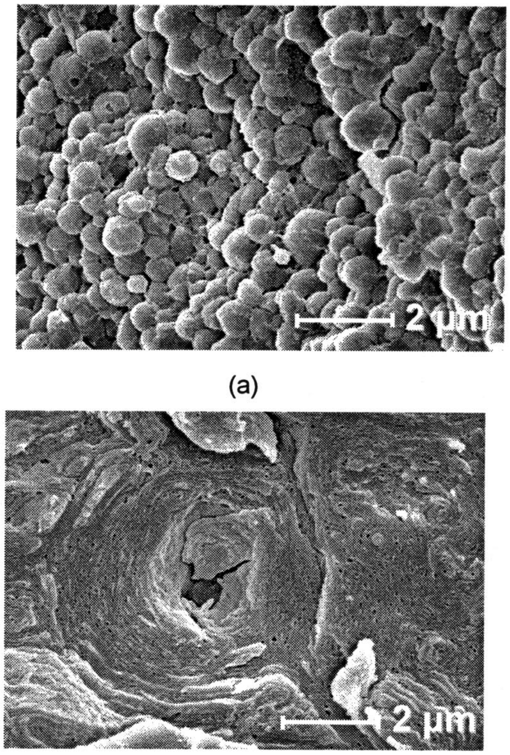


Figure 4. Typical X-ray diffraction orientation scattering profiles (intensity vs. azimuthal angle, χ), for the processing of LAS alone in the MPR.

Data (integrated over 2.6–3.3° 2θ, using a step size of 0.1° χ) are shown for process temperatures of 25°C and 60°C after processing for 20 and 30 min., respectively.



(a)

(b)

Figure 5. SEM images of LAS alone after shearing to steady state in the MPR.

Process temperatures: (a) 25°C (after 1 h shear); (b) 60°C (after 30 min shear).

torially, but only those not oriented with the flow will give "meridian" scattering (that is, $\chi = 0°$ and 180°). Near the capillary wall, the lamellae will align strongly with the wall. The X-ray beam is about 1 mm in dia. and the capillary 2 mm in dia. central alignment is only approximate. We, therefore, expect to see a mixture of scattering from the center and near-wall of the capillary. Scattering near the wall will, therefore, only be observed from the walls parallel to the X-ray beam and will give equatorial scattering; scattering will be very strong since all lamellae are expected to be well-aligned for the Bragg condition in this case.

SEM images of processed LAS (Figures 5a and 5b) confirm that the paste possesses very different microstructures after processing at 25°C and 60°C. It is evident that processing LAS at 25°C results in a microstructure of densely packed MLVs (ca. 800 nm in diameter), which is not observed when LAS is processed at 60°C. These findings are similar to those reported by McKeown (2001), although the reported MLV diameter in that case was ca. 350 nm.

Effect of additives and temperature during processing in the MPR

LAS paste was again processed at 25°C and 60°C, but with the addition of 10 wt. % sodium disilicate powder. Figure 2b shows the differential pressure data for these conditions. Figures 6a and 6b are X-ray diffraction patterns taken after 30 min of processing, while Figure 7 is of the intensity vs. χ plots and Figures 8a and 8b show SEM images of the materials processed for an hour.

The differential pressures obtained for both the pastes processed with sodium disilicate at 25°C and 60°C (Figure 2b) are similar in magnitude after about 30 min processing time. The ΔP_p values for LAS processed with sodium disilicate at 60°C are much higher than those observed in the absence of this additive (Figure 2a). It is evident that the rheological response from LAS processed at 60°C is very different depending on whether the processing is carried out with sodium disilicate or not; the steady-state differential pressure values differ by more than an order of magnitude.

From the X-ray diffraction patterns (Figure 6) and intensity vs. χ graphs (Figure 7), it can be seen that an even distri-

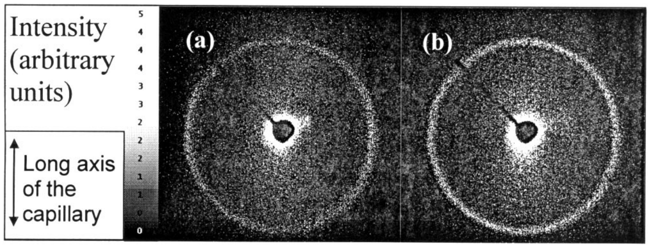


Figure 6. X-ray diffraction patterns of LAS with 10 wt. % sodium disilicate, collected after 30 min of shear in the MPR.

Process temperatures: (a) 25°C; (b) 60°C.

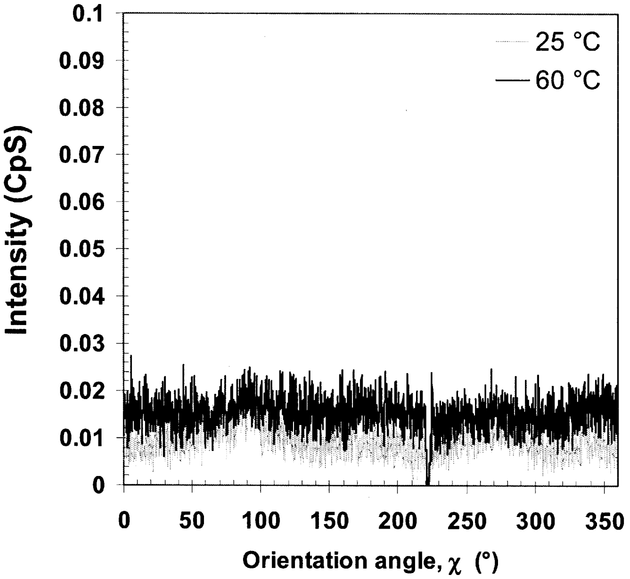


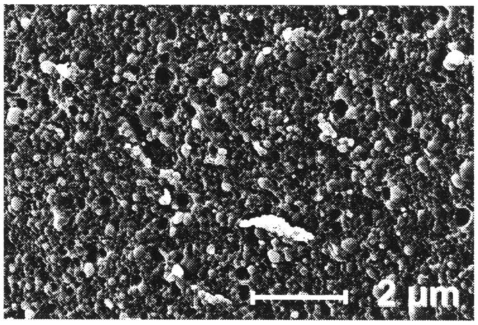
Figure 7. Typical X-ray diffraction orientation scattering profiles (intensity vs. azimuthal angle, χ), for LAS processed with 10 wt. % sodium disilicate, collected after 30 min of shear in the MPR.

Data (integrated from 2.6–3.3° 2θ, using a step size of $0.1°\chi$) are shown for process temperatures of 25°C and 60°C.

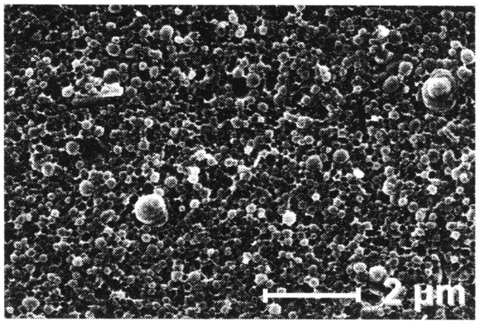
bution of scattered X-rays occurs over values of χ for the processing of LAS with sodium disilicate at 25°C, as well as 60°C. This is due to the formation of a MLV microstructure in both cases. As expected, the overall intensity of X-rays detected from scattering of LAS alone is greater than when sodium disilicate is included, because the sodium disilicate increases the absorption of X-rays.

The SEM images (Figure 8) confirm the presence of densely packed MLVs for LAS processed with sodium disilicate at both process temperatures. Thus, the strong rheopectic behavior observed for these pastes and the large resistance to flow ("stiffness") exhibited can be attributed to the packed MLV structures present. Qualitatively, these pastes appear "structured." While the formation of MLVs can be brought about at 25°C by shear alone, at 60°C, shear alone is not sufficient and sodium disilicate is needed. Even at 25°C, the presence of sodium disilicate facilitates MLV formation at the expense of lamellar structures. X-ray diffraction patterns to determine the fundamental bilayer spacings indicate that the addition of sodium disilicate may contribute to a slight decrease in the bilayer repeat distance by ca. 0.5 Å; however, further experiments are needed to confirm this. There has been no evidence for solid sodium disilicate particles in the sheared material; this is expected, as sodium disilicate is soluble in water and is likely to have dissolved in the LAS paste.

Densely packed MLV structures can occur with or without the presence of sodium disilicate, depending on the process temperature and conditions. Sodium disilicate does, however, appear to promote smaller, more spherical and tightly packed MLVs. Comparison of SEM images of LAS processed at 25°C (Figure 5a), 25°C with sodium disilicate (Figure 8a) and 60°C with sodium disilicate (Figure 8b) illustrate this.



(a)



(b)

Figure 8. SEM images of LAS with 10 wt. % sodium disilicate processed for 1 h in the MPR.

Process temperatures: (a) 25°C; (b) 60°C.

Preliminary experiments indicate that a similar effect to that achieved by adding sodium disilicate can also be achieved by adding sodium chloride. We, therefore, speculate that MLV formation is promoted by raising the ionic strength of water present in the LAS bilayers. This may change the effective head-group size of the LAS molecule or change the electrostatic forces within and between layers. This will be further discussed in a future publication.

Effect of processing time in the MPR

Figures 9a, 9b, 9c, and 9d are SEM images of LAS sheared at 25°C with 10 wt. % sodium disilicate for 7 min, 1 h, and 3 h 45 min, respectively. A typical differential pressure curve for these processing conditions can be seen in Figure 2b.

After 7 min of processing, a biphasic state exists, as both planar lamellar structures and MLVs are present. It is also evident that the planar lamellae are orientated (Figure 9b)—aligned with the minimum surface area facing the direction of flow. The planar surfaces of the lamellae lie parallel to the plane of the MPR capillary walls.

With longer processing times, the planar lamellae are destroyed and form MLVs. A longer shearing time also results in the MLVs becoming more uniform in size as the larger MLVs are broken down. The bilayer repeat distance does not change during 50 min of shear, as X-ray evidence (not included in this article) has shown. Thus, the change in size of

MLVs during processing appears to involve the "peeling off" of the outer lamellar layers, while the inner MLV layers remain intact. It is plausible that the increase in stiffness (resistance to flow) exhibited with processing time (Figure 2b) is due to the increasing number of small MLVs: the energy required to overcome frictional forces between the MLVs would be greater due to the increase in surface area.

Stability of processed LAS paste over time

In order to investigate the stability of processed pastes with a MLV microstructure, a sample of LAS was processed in the MPR at 25°C with 10 wt. % sodium disilicate for ca. 3 h and 45 min and then left for eight days in a sealed vial before SEM images were taken. Figures 10a and 10b are images of the "aged"paste at different magnifications. It is evident from the SEM images that the MLV structures co-exist with another type of microstructure (Figure 10a); these "lamellar clusters" form uniformly throughout the paste (Figure 10b), and are not observed in freshly processed pastes. The lamellar clusters that appear during storage of processed LAS paste have lamellae that are not aligned in any particular direction unlike the orientated lamellae that are present during shear flow (Figure 9b).

From qualitative observations, "structured" paste is increasingly soft and sticky with storage time. The destruction of MLVs and return to the planar lamellar state by way of lamellar cluster formation is a likely explanation for this phenomenon.

The MLVs formed during LAS processing are metastable. The application of shear must shift the equilibrium so that MLV formation is favored. With the removal of shear, the planar lamellar phase again becomes the equilibrium state, thus rendering the MLVs metastable.

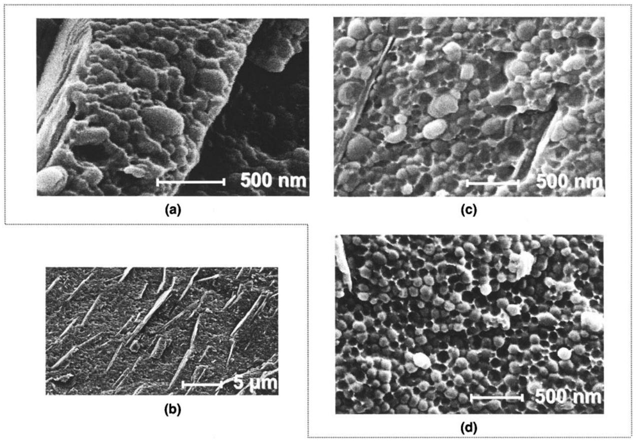


Figure 9. SEM images of LAS processed at 25°C with 10 wt. % sodium disilicate in the MPR.

Processing time: (a) and (b) 7 min (at different magnifications); (c) 1 h; (d) 3 h and 45 min. Orientation of planar lamellae is evident in (b).

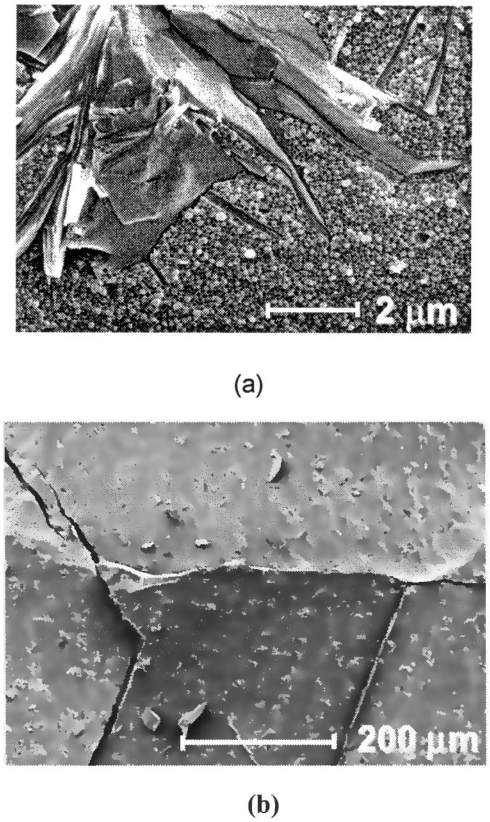


Figure 10. LAS paste processed at 25°C with 10 wt. % sodium disilicate in the MPR for ca. 3 h and 45 min.

SEM images at different magnifications (a) and (b) were taken after the sample was stored in a sealed vial for eight days—"lamellar clusters" and MLV structures are identifiable.

Conclusions

In the 78 wt. % LAS paste system studied, it was found that processing parameters such as temperature, the presence of additives, and processing time have a significant effect on shear-induced structures, such as MLVs. LAS paste with a densely packed MLV microstructure is hard and stiff, whereas LAS in the planar lamellar phase is softer and stickier. "Structured" paste, as it is referred to in industry, refers to paste with a packed MLV microstructure and is used in the manufacture of compact detergent powders by agglomeration, whereas "unstructured" (planar lamellar) paste is suitable for being pumped through pipes for transport purposes.

Although MLVs can be formed at a process temperature of 25°C whether additives were used or not, at 60°C, sodium disilicate is necessary. The addition of sodium disilicate extends the region in the LAS phase diagram where the formation of MLVs is possible. MLVs processed with sodium disilicate were smaller, more spherical and tightly packed than MLVs formed without the additive. Pastes processed with sodium disilicate also appeared harder and exhibited a greater resistance to flow.

During the transition from planar lamellae to MLVs, when both types of structures are present, the lamellae orientate parallel to the flow. With increased processing time, more of the planar lamellae are destroyed to form MLVs and the size of the MLVs decreases and becomes more uniform.

"Structured" paste showed aging, reverting from being hard and stiff to being soft and sticky with time. This change in properties was due to the metastable nature of the MLVs in the absence of shear, and the transition back to the initial planar lamellar state by the formation of "lamellar clusters". This is an important consideration when using "structured" paste in industrial processes.

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Literature Cited

Aouad, Y. G., J. L. Vega, and L. Goovaerts, "Chemical Structuring of Surfactant Pastes to Form High Active Surfactant Granules," European Patent Specification, EP No. 0 508 543 B1 (1997).

Aouad, Y. G., and H. G. W. Dickenson, "Process for Preparing Detergent Granules," European Patent Specification, EP No. 0 663 439 B1 (2000).

Auernhammer, G. K., H. R. Brand, and H. Pleiner, "The Undulation Instability in Layered Systems Under Shear Flow—A Simple Model," *Rheol. Acta.*, **39**, 215 (2000).

Bagley, E. B., "End Corrections in the Capillary Flow of Polyethylene," *J. Appl. Phys.*, **28**, 624 (1956).

Bergmeier, M., M. Gradzielski, H. Hoffmann, and K. Mortensen, "Behavior of Ionically Charged Laminar Systems under the Influence of a Shear Field," *J. Phys. Chem. B.*, 103, 1605 (1999).

Diat, O., and D. Roux, "Preparation of Monodisperse Multilayer Vesicles of Controlled Size and High Encapsulation Ratio," *J. Phys. II France*, **3**, 9 (1993).

Diat, O., D. Roux, and F. Nallet, "Effect of Shear on a Lyotropic Lamellar Phase," *J. Phys. II France*, **3**, 1427 (1993).

Helfrich, W., "Lyotrophic Lamellar Phases," *J. Phys. Condens. Matter*, **6**, A79 (1994).

Holland, F. A., and R. Bragg, *Fluid Flow for Chemical Engineers*, 2nd ed., E. Arnold, London (1995).

Le, T. D., U. Olsson, and K. Mortensen, "Topological Transformation of a Surfactant Bilayer," *Physica B*, **276**, 379 (2000).

Le, T. D., U. Olsson, and K. Mortensen, "Packing States of Multilamellar Vesicles in a Nonionic Surfactant System," *Phys. Chem. Chem. Phys.*, **3**, 1310 (2001).

Le, T. D., U. Olsson, K. Mortensen, J. Zipfel, and W. Richtering, "Nonionic Amphiphilic Bilayer Structures Under Shear," *Langmuir*, **17**, 999 (2001).

Léon, A., D. Bonn, J. Meunier, A. Al-Kahwaji, O. Greffier, and H. Kellay, "Coupling Between Flow and Structure for a Lamellar Surfactant Phase," *Phys. Rev. Lett.*, **84**(6), 1335 (2000).

Lukaschek, M., S. Müller, A. Hansenhindl, D. A. Grabowski, and C. Schmidt, "Lamellar Lyomesophases Under Shear as Studied by Deuterium Nuclear Magnetic Resonance," *Colloid Polym. Sci.*, **274**, 1 (1996).

Mackley, M. R., R. T. J. Marshall, and J. B. A. F. Smeulders, "The Multipass Rheometer," *J. Rheol.*, **39**(6), 1293 (1995).

McKeown, S. A., "The Structure and Rheology of a Commercial Surfactant-Based System," PhD Thesis, University of Cambridge, U.K. (2001).

McKeown, S. A., M. R. Mackley and G. D. Moggridge, "Shear-Induced Structures in a Commercial Surfactant System: Effect of Temperature and Additives," *Trans. IChemE Part A*, (July 2003).

Matheson, K. L., "Physical Properties and Behaviour of Linear Alkylbenzenesulfonates in Mixtures with Other Surfactants in Household Detergent Products," *Anionic Surfactants: Organic Chemistry*, H. W. Stache, ed., Surfactant Science Series, Vol. 56, Marcel Dekker, New York, pp. 110–140 (1996).

Mortensen, K., "Structural Studies of Lamellar Surfactant Systems Under Shear," *Curr. Opin. Colloid Interface Sci.*, **6**, 140 (2001).

Schmidt, G., S. Müller, C. Schmidt, and W. Richtering, "Rheo-optical Investigations of Lyotropic Mesophases of Polymeric Surfactants," *Rheol. Acta*, **38**, 486 (1999).

Schmidt, G., S. Müller, P. Lindner, C. Schmidt, and W. Richtering, "Shear Orientation of Lyotropic Hexagonal Phases," *J. Phys. Chem. B*, **102**, 507 (1998).

Zilman, A. G., and R. Granek, "Undulation Instability of Lamellar Phases under Shear: A Mechanism for Onion Formation?" *Eur. Phys. J. B*, **11**, 593 (1999).

Zipfel, J., P. Lindner, M. Tsianou, P. Alexandridis, and W. Richtering, "Shear Induced Formation of Multilamellar Vesicles (Onions) in Block Copolymers," *Langmuir*, **15**, 2599 (1999).

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