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A study of the physical properties of lamellar liquid-crystalline dispersions

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

1993

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Pas, J. C. V. D. (1993). *A study of the physical properties of lamellar liquid-crystalline dispersions*. s.n.

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SUMMARY

Surfactant-structured liquid detergent products are lamellar liquid-crystalline dispersions in an aqueous electrolyte solution. Lamellar dispersions should be physically stable and readily pourable in order to be used as liquid detergents, *i.e.* they must not show phase separation during storage and must have a low viscosity. Mixing of the main components of liquid detergents, surfactants and electrolytes, in water may lead to lamellar dispersions. However, not all the lamellar dispersions are physically stable, pourable systems. Important questions addressed in this thesis are (i) which are the factors governing the physical stability of these dispersions and (ii) what is the relation between the chemical composition of the surfactant and the physical stability of these systems as a function of electrolyte type and concentration. There is an ongoing need for concentrating liquid detergents. For that reason, but also because polymers are becoming increasingly important as ingredients in liquid detergent products, the effect of polymers on the physical properties of lamellar dispersions has been investigated. Two types of polymers have been studied: polymers which are and which are not attached to the lamellar droplets. In colloid chemistry they are called "anchored" and "free" polymers, respectively.

In chapter 1 the reader is introduced to the different aggregate morphologies in which surfactant molecules may aggregate in aqueous solution. The relation between the architecture of a surfactant molecule and the morphology of the aggregate is expressed in terms of a molecular packing parameter. Furthermore, the different types of lyotropic liquid-crystalline phases and the factors involved in the transition of one type of lyotropic liquid-crystal to another is discussed. Special attention is paid to the lamellar (liquid-crystalline) phase, both as a single phase and as a dispersed phase, and the different forms in which these phases can be manifested. The occurrence of liquid-crystalline phases in everyday life is emphasised with a focus on the importance of these phases in the "world of detergent products". The relevance of lamellar phase dispersions, consisting of the four components anionic surfactant, nonionic surfactant, water and electrolyte, as model systems for surfactant-structured liquid detergents is indicated.

In the second chapter the phase behaviour and physical stability of a number of these four component model systems are described. Pseudo-binary phase/stability diagrams, *i.e.* surfactant ratio at constant surfactant concentration versus salt concentration, of the systems frequently examined in this thesis are introduced. The phases are characterised using light and electron microscopy, conductivity, centrifugation experiments and by the visual appearance of the systems. They are characterised as lamellar and/or isotropic phases. The picture, often described in the literature, for a "continuous" lamellar phase in terms of a stack of planar bilayers throughout the whole sample, is an oversimplification. From our experimental data it follows that a "continuous" lamellar phase should be described as a mixture of planar and spherically-layered structures in which either of them can dominate. The dispersed lamellar phase in the two-phase systems can be viewed as "lamellar droplets", defined as multi-lamellar vesicles with bilayers extending (almost?) to the centre of the droplet. Furthermore, it has been found that in a lamellar plus isotropic two-phase system the volume fraction of the lamellar phase can be determined both from centrifugation experiments and conductivity measurements. The results of both methods are in fair agreement. It is proposed that the

change in morphology of the lamellar structure from a "continuous" lamellar phase (planar bilayers) to a lamellar dispersion (curved bilayers) is governed by a complex balance between a number of intra- and interbilayer interaction forces, while the mechanical treatment of the system can also have an effect. Possibly as a result of this situation and of the broad mixture of molecular structures in the present systems, only gradual morphology changes in the lamellar phase area are detected.

In chapter 3 the dependence of the physical stability of lamellar dispersions on electrolyte type and concentration is analysed. Physical stability is obtained when the volume fraction of the lamellar phase is larger than approximately 0.6, preferably larger than 0.7, and when the lamellar droplets do not flocculate. The volume fraction of the lamellar phase, at a given surfactant concentration, depends on the water layer thickness. The water layer thickness, in turn, depends on the interaction forces between the bilayers. The same interaction forces which govern the thickness of the water layers also determine the propensity for flocculation of the lamellar droplets. Furthermore, at relatively low electrolyte concentrations, the presence of surfactant micelles can induce flocculation of the lamellar dispersion. It has been found that the osmotic repulsion between the poly(oxyethylene) headgroups of the nonionic surfactant is the dominating interaction for obtaining a sufficiently thick water layer and a sufficiently large volume fraction of the lamellar phase for physical stability. An important parameter in this context is a sufficiently good quality of the solvent (salt solution) for the nonionic headgroups. This is also one of the requirements for preventing flocculation of the lamellar droplets. In addition, the salt concentration should be high enough to reduce the number of surfactant micelles below the limit for inducing flocculation of the lamellar droplets. Type and concentration of the salts govern both the solvent quality for the nonionic surfactant headgroups and the number of surfactant micelles in the continuous phase of the lamellar dispersion.

The study of the dependence of the physical stability of lamellar phase systems on electrolyte type and concentration was extended to a wider range of salting-out electrolytes in chapter 4. Much more emphasis has been placed on the role which the type of surfactant can play in affecting the physical stability of the lamellar system in the presence of high concentrations of strong salting-out electrolytes. The salting-out effectiveness of electrolytes for nonionic surfactants and the effect on the physical stability of lamellar phase systems were examined more quantitatively. It was shown that there is a correlation between (i) the electrolyte concentration necessary to induce salting-out/phase separation of a micellar solution of the surfactant and (ii) the maximum electrolyte concentration which can be incorporated into a lamellar phase system formed from the surfactant before physical instability is observed. Furthermore, it was demonstrated that even at high concentrations of strong salting-out electrolytes physically stable lamellar phase systems can be obtained. This can be achieved when the nonionic poly(oxyethylene) surfactant is (partly) replaced by a surfactant which has a higher resistance against salting-out effects.

The effects of "free" and "anchored" polymers (see above) on the physical properties of lamellar dispersions have been examined in detail. Addition of free polymers to lamellar dispersions (chapter 5) may lead to osmotic compression (decrease of the volume fraction of the lamellar phase), depletion flocculation and fusion of lamellar droplets. Osmotic compression will occur if the size of the polymer coil (*e.g.* the molecular weight) is too large with respect to the thickness of the lamellar water layer. In analogy with "normal" dispersions, the polymer concentration at which depletion flocculation is initiated in lamellar

dispersions decreases droplets, with a concentration lower than observed. However, concentration for depletion flocculation of the viscosity of the dispersions while retaining an increased viscosity.

Chapter 6 deals with lamellar dispersions using the nonionic surfactant between the layers instead of droplets, an osmotic pressure inside the lamellar phase. Consequently, thin lamellar layers have been found that these (i) are anchored in the well hydrated in the outer layer of the lamellar phase. The acrylate-co-lauryl methacrylate hydrophobic side-chain is strongly hydrophilic. The ratio in the copolymer of the hydrophilic polymers which fulfil the requirements for a physically stable lamellar phase in the presence of electrolyte and surfactant. These systems which are also able to form lamellar droplets, this is due to the connections between the droplets in a strong increase in viscosity.

In the final chapter practical applications are discussed.

dispersions decreases with increasing molecular weight of the polymer. Fusion of lamellar droplets, with a concomitant increase in lamellar droplet size, already occurs at polymer concentrations lower than the polymer concentration at which depletion flocculation is observed. However, extensive fusion is only observed well above the critical polymer concentration for depletion flocculation. Osmotic compression and fusion result in a decrease of the viscosity of the lamellar dispersions and allow for concentration of the lamellar dispersions while retaining pourability. Depletion flocculation results in physical instability and an increased viscosity of the systems.

Chapter 6 deals with the effects of anchored polymers on the physical properties of lamellar dispersions under poor solvent conditions for the poly(oxyethylene) headgroups of the nonionic surfactants (high electrolyte concentration). Because of the similarity in structure between the layers inside one lamellar droplet and between the outer lamellae of two adjacent droplets, an osmotic attraction takes place between, on the one hand, the lamellar layers inside the lamellar droplets *and*, on the other hand, between adjacent lamellar droplets. Consequently, thin lamellar water layers and flocculated lamellar droplets are obtained. It has been found that these *coupled* interaction forces can be *decoupled* by using polymers which (i) are anchored in the layers of the lamellar droplets, (ii) have hydrophilic parts which are well hydrated in the concentrated salt solution and (iii) are predominantly anchored in the *outer layer* of the lamellar droplet. In practice this can be achieved by using *e.g.* poly(sodium acrylate-co-lauryl methacrylate), a hydrophilic polymer backbone with one or more hydrophobic side-chains (the anchors for the lamellar bilayers). The sodium acrylate backbone is strongly hydrophilic and fulfils requirement (ii). The molecular weight of and monomer ratio in the copolymer are important in dealing with requirements (i) and (iii). Using polymers which fulfil all three requirements, so-called *decoupling polymers*, colloiddally and physically stable lamellar dispersions can be obtained which are substantially concentrated in electrolyte and surfactants and which have a low viscosity. However, when polymers are used which are also able to anchor in the interior of the lamellar droplets or in more than one lamellar droplet, this may result in an increase of the volume fraction of the lamellar phase or connections between lamellar droplets by polymer bridges. In both cases this may result in a strong increase of the viscosity and decreased pourability.

In the final chapter, the main findings and conclusions are summarised and the practical applications of the work for surfactant-structured liquid detergent products are discussed.