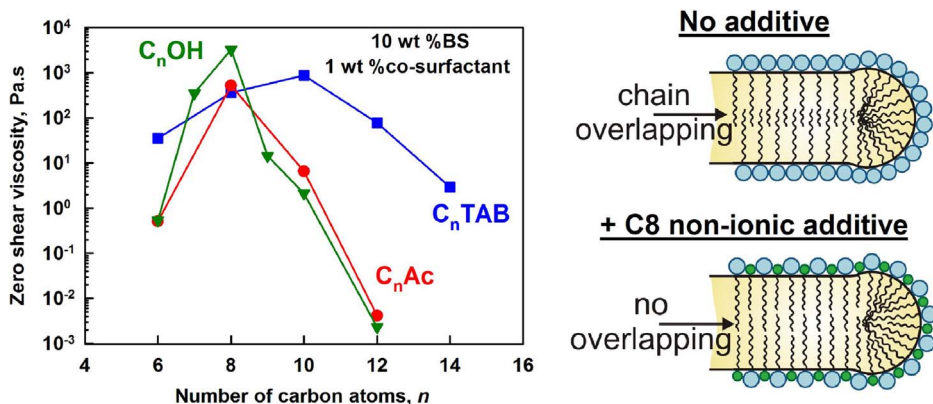# Control of surfactant solution rheology using medium-chain cosurfactants

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GRAPHICAL ABSTRACT

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ABSTRACT

The rheological properties of surfactant solutions play an important role in their applications. Here we study systematically how different cosurfactants affect the rheological properties of mixed solutions of the anionic surfactant sodium laurylether sulfate (SLES) and the zwitterionic cocoamidopropyl betaine (CAPB). Mixed SLES + CAPB solutions are used in various formulations due to their excellent foaming and cleaning properties. These solutions possess nearly Newtonian behavior and low viscosity. However, the addition of cosurfactants in low concentrations may significantly increase the viscosity of these solutions and even transform them into viscoelastic gels. Here we study systematically a wide range of ionic and nonionic cosurfactants with different head-groups, chain-lengths and structures of the hydrophobic tails (linear, branched, double bonded). We reveal an optimal chain-length of 8–10 carbon atoms of the cosurfactant molecules which ensures the highest viscoelasticity of the triple SLES + CAPB + cosurfactant solutions. Cationic cosurfactants and nonionic ones with small head-group (e.g. fatty alcohols and fatty acids) are most efficient in increasing the solution viscoelasticity. There is a hierarchy in the parameters of the cosurfactant molecules which govern this behavior − most important is the head-group charge, then the chain-length and, finally, the presence of branching and double bonds in the hydrophobic tails. The observed trends are explained with the effect of the cosurfactant molecules on the properties of the entangled wormlike micelles formed in these solutions.

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1. Introduction

Concentrated micellar solutions find applications in various industries and consumer products. Usually, there are specific requirements to their rheological properties, e.g. in dish-washing detergents and personal care products. One approach to control these properties is to ensure the formation of entangled wormlike micelles (WLM) which increase the solution viscosity and may even lead to the appearance of certain viscoelasticity of the solutions [1]. The micellar shape is governed primarily [2] by the packing parameter, $p = v/(a_0 l_c)$, which depends on the surfactant molecular characteristics: the molecule volume, v, the area-per-molecule, a_0, and the length of the hydrophobic tail, l_c. Increasing this parameter above $p = 1/3$ leads to change in the micellar shape from spherical to rod-like and, eventually, to worm-like micelles with the related increase of solution viscosity and elasticity [3,4]. The theoretical models [5–11] which relate the micellar properties (such as shape, length and various relaxation times) with the overall rheological properties of the respective micellar solutions are briefly explained in Section 3 below and are used to interpret our experimental data.

There are several approaches to increase the packing parameter and to induce the formation of wormlike micelles. One possibility is to decrease the area of the surfactant head-group. With ionic surfactants this approach is often realized by adding electrolytes of high concentration [12,13]. The electrolytes screen the electrostatic repulsion between the head-groups of the neighboring molecules in the micelles and, thus, lead to the formation of more compact head-group arrangement on the micelle surface. Similar effect is observed when mixing oppositely charged ionic surfactants, e.g. cationic and anionic surfactants, or cationic/anionic with zwitterionic surfactants [14]. For ethoxylated nonionic surfactants, the area per head-group depends on the number of ethoxy groups in the surfactant head-group. For example, in the work of Acharya et al. [16] it is shown that there is an optimal number of EO groups which leads to highly viscous solutions of the SDS + C12EO3 mixture.

Another approach to vary the packing parameter is to increase the volume of the hydrocarbon fraction of the surfactant molecules. Well known examples are the double-tailed lipids which tend to form planar self-assembled structures due to the doubled volume, v, at (almost) fixed a_0 and l_c [2].

Several papers studied the effect of cosurfactant chain-length on the micellar solutions of sucrose esters. Thus, Aramaki et al. [16] studied the effect of alcohol cosurfactants with chain-length varied between C3 and C9, on the viscosity of sucrose monohexadecanoate solutions, viz. for a main surfactant with C16 alkyl chain. They showed that the longer-chain alcohols are more efficient to increase the viscosity of such solutions. However, the cosurfactant chain-length was limited to 9 carbon atoms in these studies, because precipitates were formed and phase separation was observed at longer chain-lengths of the alcohols.

In a separate study [17], the same group analyzed the effect of fatty acids (FAc) with chain-length varied between C6 and C12. An optimal ratio between FAc and sucrose monopalmitate was observed and the highest viscosity was obtained when using fatty acids with 10 and 12 carbon atoms (C10Ac and C12Ac). In addition, these authors showed that changing the lauric acid into sodium laurate increases solution viscosity, due to electrostatic repulsion between the micelles and to the related "excluded volume" effect.

In another study, Raghavan et al. [18] showed for oppositely charged surfactants that the solution viscosity increases when increasing the asymmetry between the alkyl chains of sodium oleate (NaOA) and alkyltrimethylammonium bromide (CnTAB). The largest effect was observed for C8TAB. In Ref. [19], the effect of chain-length of various CnTABs on the micellar solutions of C16TAB was studied in the presence of KBr. The results showed that increasing the fraction of shorter-chain additive leads to lower solution viscosity, due to formation of micelles with shorter persistence length and higher flexibility. These results were explained with reduced van der Waals attraction

between the surfactant-cosurfactant tails with different lengths which, in turn, leads to less compact and less stable micelles.

Kamada et al. [20] studied the mixture of SDS + C12EO3 (as main surfactants) and found a maximum in the solution viscosity at a certain SDS to C12EO3 ratio. In the presence of cosurfactants (e.g., polar fragrance molecules) this maximum is shifted toward other ratios of the two main surfactants. These authors explained their results with solubilization of the polar cosurfactant molecules in the palisade layer, which changes the curvature of the micellar surface and, thus, shifts the surfactant ratio corresponding to maximum solution viscosity.

Parker and Fieber [12] studied the effect of cosurfactants (fragrances and other short- chained additives) on solution of SLES-2EO, in the presence of NaCl. In this system, a maximum in the viscosity is observed at a certain NaCl concentration. The authors showed that the addition of fragrance or oily cosurfactants can change the magnitude and/or the position of the viscosity maximum which is also explained with the solubilization of the cosurfactant molecules and the related change in the micelle flexibility (persistent length).

In our previous study [21] we reported that medium-chain fatty acids (C8 and C10 FAc) induce the formation of wormlike micelles when added to mixed surfactant solutions of SLES + CAPB. The triple solutions exhibit viscoelastic rheological response [21], while the double solutions of SLES + CAPB have low viscosity and (almost) Newtonian behavior. In contrast, the longer chain fatty acids (C12 to C18 FAc) have no such effect on solution rheology [21]. This phenomenon was explained with the mismatch between the hydrocarbon tails of the main surfactants (containing mainly C12 chains) and the cosurfactants with C8 or C10 tails. This mismatch seems to be essential for the formation of wormlike micelles, when cosurfactant is added in this system.

In an independent series of papers, Kralchevsky et al [22,23]. observed a well pronounced peak in the solution viscoelasticity, when varying the concentration of the cosurfactants (fatty acids added to SLES + CAPB mixture) and used electron cryo-microscopy to clarify how the peak position and height are related to the transformations in the micellar shape and size.

The aim of the current paper is to study systematically how the cosurfactant molecular parameters affect the rheological behavior of SLES + CAPB solutions. We show that highly viscous and viscoelastic solutions could be formed by adding several classes of cosurfactants which differ substantially in their molecular characteristics. We observe a clear hierarchy in the parameters of the cosurfactant molecules which govern this rheological transition – most important is the cosurfactant head-group charge, followed by its chain-length and, finally, the presence of branching and double bonds in the hydrophobic tails. An optimal chain-length of 8–10 carbon atoms of the cosurfactant molecules is revealed, independently of the specific cosurfactant head-group, which ensures the highest viscoelasticity of the triple SLES + CAPB + cosurfactant solutions. These trends are explained by analyzing the effects of the cosurfactants on the properties of the wormlike micelles formed in these solutions.

The paper is organized as follows: In Section 2 we describe the materials and methods used. In Section 3 we present the main experimental results. Their molecular interpretation is described in section 4. The main conclusions are summarized in section 5.

2. Materials and methods

2.1. Materials

The basic surfactant system, denoted hereafter as BS, is a mixture of sodium lauryl ether sulfate, SLES (product of Stepan Co., IL, USA, with commercial name STEOL CS-170, which contains around 1 EO group per molecule on average) and cocoamidopropyl betaine, CAPB (product of Goldschmith, commercial name Tego Betaine F50). The concentration of the main surfactants in the studied solutions was 10 wt% of