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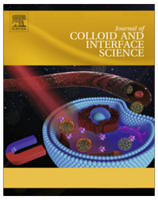

Regular Article

The effect of solvent polarity on wormlike micelles using dipropylene glycol (DPG) as a cosolvent in an anionic/zwitterionic mixed surfactant system

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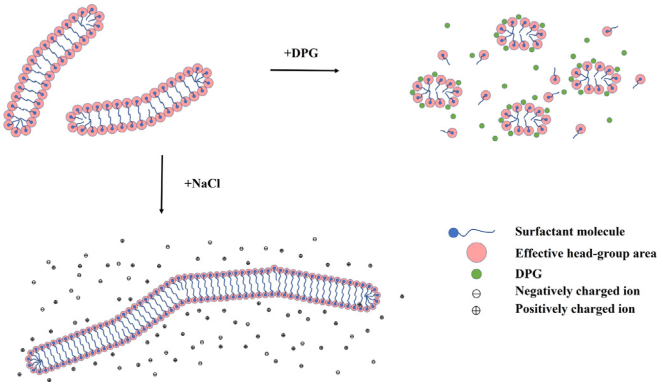
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: The behavior/properties of micellar solutions are governed by Coulombic interactions that are influenced by the polarity of the surfactant head groups, hydrophobic tails, and solvent molecules. The addition of co-solvent should have a direct impact on solvent polarity and the size of the micelles are expected to decrease accordingly.
Experiments: In this study, a mixed surfactant system is studied composed of a common anionic surfactant, sodium laureth sulfate-1, modified by a zwitterionic surfactant, cocamidopropyl betaine in deuterated water. In this system, worm-like micelles (WLMs) are formed. The influence of a co-solvent, dipropylene glycol (DPG) in the present of high salt content, is investigated. DPG primarily modifies the dielectric constant of the solvent.
Findings: It was found that the addition of DPG slightly decreased the micelle radius, but dramatically reduced the persistence length as well as the contour length of the micelles. The relative dependence of contour length on salt concentration is not significantly changed. Thus, it is shown that the self-assembled structure can be tuned by adjusting solvent polarity without affecting the relative tunability of the WLM/ellipsoidal structure through counter ion concentration.

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1. Introduction

Amphiphilic molecules in aqueous solutions can self-assemble into elongated, semi-flexible aggregates, also known as worm-like micelles (WLMs) [1]. The ability to reversibly self-assemble gives unique properties to WLMs and has led to widespread application [2]. As the behavior/performance of the WLM products depend largely on the self-assembled nanostructure, it is important to control the dynamic equilibrium between the self-assembled state and dispersed surfactant molecules. The main idea of manipulating the equilibrium is to control the balance between solvent incompatibility with the tail groups, which drives the formation of micelles, and solvent electrostatic interactions with the head groups which favor the dispersion of surfactant molecules [3]. Co-solvents/co-surfactants have long been employed to alter the dynamic balance of micellar systems [7] and the performance of surfactants, such as in pharmaceutical formulation [4] and oil recovery [5,6]. For example, in oil recovery [5,6], formulas modified by co-solvents show increased oil recovery with reduced viscosity and surface tension. Economically efficient and environmental friendly features are also reasons that co-solvents/co-surfactants are extensively used.

Non-aqueous polar molecules, glycols or alcohols, are of particular interest as co-solvents/co-surfactants due to their relatively high dielectric constant, cohesive energy density and their ability to form hydrogen bonds with water molecules [8]. The term co-solvent or co-surfactant is chosen depending on the solubility of the alcohol in water and their consequent partitioning into the micelle or solvent phase. Usually, short chain alcohols with higher polarity tend to stay in the water phase [10]. The decrease of micelle size upon addition of this kind of alcohol is explained by the change of solvent properties. Thus, short chain alcohols are usually considered as co-solvents. Alcohol molecules with longer alkyl chains tend to show weaker polarity [9] that leads to poor miscibility of long chain alcohols in water and their increasing partition into the micellar phase. Long chain alcohols are often considered co-surfactants.

In order to understand the impact of co-solvents on micellar systems, two main aspects have been studied, the critical micelle concentration (CMC) and the size of the micelles. Different combinations of nonionic surfactant, ionic surfactant, and mixed surfactant have been studied [8,10–19]. As a key parameter of micellization, the CMC is defined as the concentration above which micelles form. Further added surfactant goes directly into the micellar phase while the concentration of surfactant monomers remaining dispersed in the solution is more or less constant at the CMC [20] in a dynamic equilibrium between micelles and free surfactant monomers [21]. Upon addition of a non-aqueous, polar co-solvent, the reduced hydrophobic interaction between the surfactant tails and solvent molecules leads to an increase in the solubility of free surfactant monomers relative to micelles thus shifting the CMC to a higher value. Such an increase in the CMC has been extensively observed [8,10–17]. In addition to an increase in the CMC, a decrease of the micellar size was reported in these studies. This increase in size was associated with increased surface curvature due to larger incompatibility between the head groups and solvent, and a concomitant increase in repulsion between the charged head groups [8,10–17]. However, this is not a universal observation and the explanation does not apply to all systems. Others report a reverse trend that the size of micelles increase with the addition of co-solvents. Penfold, Alexandridis et al. [18,19] reported an increase in micelle size and a lower concentration onset of CMC of surfactant systems with increasing co-solvent concentration using small angle neutron scattering (SANS). This contrary trend was explained by the dehydration of the surfactant head groups due to the relatively low polarity of the co-solvent molecules, which caused a reduction of the effective head group area and led to an increase in the micelle diameter due to a lower surface curvature. No clear boundary was drawn between the two tendencies. The actual impact of a certain type of co-solvent on a specific micelle system still remains elusive, which makes the study of individual cases necessary. Furthermore, although numerous experiments have been conducted on this topic, most of the research was confined to spherical micelles. A fundamental understanding of the effect of co-solvents on WLMs is still very limited.

In this work, it was chosen to study the diol dipropylene glycol (DPG) as a co-solvent in a mixed surfactant system with high salt content. DPG is a commonly used stability modifier for detergents due to its low toxicity and relatively high dielectric constant. The addition of glycol to the aqueous phase leads to a decrease in the dielectric constant, and the cohesive energy density, as well as breakup of the water structure [22]. The decrease of the dielectric constant enhances the long-range electrostatic interactions between charged head groups and solvent disproportionally. In this paper, solvent dielectric characteristics are considered as a key factor that could alter the micellization process. Neutron scattering is used to quantify structural changes associated with changes in solvent polarity.

Upon addition of counterions, screening of electrostatic repulsions between headgroups leads to a decrease in effective headgroup area. At high counterion concentrations, spherical micelles transition through ellipsoidal, rod-like, and worm-like structures that display a diameter, persistence length, and contour length rather than the single size associated with a spherical micelle. The transition between spherical and ellipsoidal micelles in surfactant concentration is sometimes called a second CMC [23]. Adjustment of salt concentration is often used to control the contour length and viscoelastic properties of WLMs [24]. Previous studies in water-alcohol systems have been limited to studies of micellization of spherical micelles in terms of the CMC. The impact on WLM structures with high counter ion concentrations and the impact of solvent polarity on counter ion control of WLM structure are absent from the literature.

In this paper, we investigate the change of WLM/ellipsoidal structure due to a change in solvent polarity using SANS. DPG was selected as a co-solvent due to its extensive use in industrial formulations of cosmetic products. The aim of this work is to understand the effect of solvent polarity on the structure of WLMs at high salt content and to observe its effect on control over WLM contour length and viscoelastic properties through variation in salt concentration with mixed surfactants.

2. SANS model for WLM structure

Above the CMC, formation of spherical micelles occurs. A secondary CMC is observed at the onset of anisotropic cylindrical and ellipsoidal micelles that accommodate reduced head group repulsion as counter ion screening increases with increased salt concentration. Once an asymmetric structure forms the structure is largely governed by the end cap energy relative to the energy of the cylindrical structure. High end-cap energy encourages growth of very long micelles that can be thread-like with contour lengths on the order of microns. There is a wide distribution of lengths in such a thread-like micelle population that is proposed to follow an exponential number distribution [25] similar to synthetic polymers grown from step-growth polymerization.

Worm-like chains have been characterized using a persistent chain model or using a Kuhn chain model. The persistent chain model relies on a statistical description of the persistence length