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The mixing behaviour of anionic and nonionic surfactant blends in aqueous environment correlates in fatty acid ester medium

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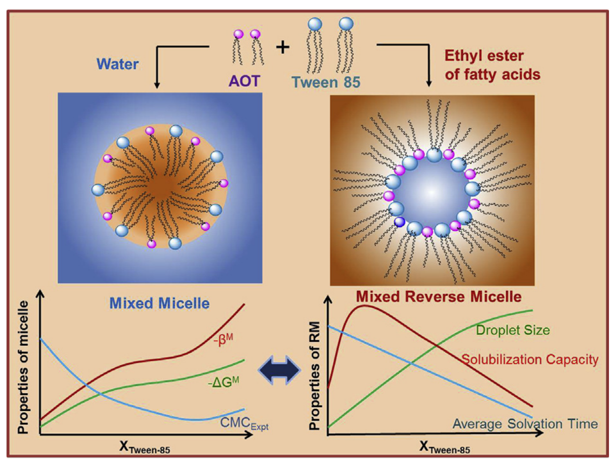
HIGHLIGHTS

- Favourable micellization with enhanced surface activity perceive for mixed AOT and Tween.
- Negative interaction parameter and large deviation from ideal CMC's indicate synergistic interaction in mixed micelle.
- Structural functionality of fatty acid ester affects reverse micellar solubilization ability.
- Solvation and rotational relaxation dynamics follow similar trend for fatty acid esters.
- Solvation dynamics collaborates well with droplet size and abundance of bulk-like water.

GRAPHICAL ABSTRACT



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ABSTRACT

Mixtures of dissimilar surfactants can have superior properties compared to those of the individual surfactant components involved, which provide impetus for research on interactions between surfactants. It was also demonstrated that a change in the composition of external phase promotes remarkable changes in interfacial properties of reverse micelles (RMs), which are crucial to understand the system in order to use them as nanoreactors. Hence, it should be achievable to explore the influence of non-ionic Tween-85 on the properties of anionic AOT based micelle as well as RMs in fatty acid esters [e.g., ethyl myristate (EM), ethyl palmitate (EP) and ethyl oleate (EO)]. A comprehensive micellization behavior is studied at different mixed compositions ($X_{Tween-85}$) by surface tension method. Non-ideal mixing behaviors along with synergistic interaction between the constituent surfactants in the mixed micelles are evidenced. Mixed micelles illustrate favorable micellization behavior in terms of thermodynamic parameters. Further, fatty acid ester medium-based mixed RM shows synergism in water solubilization capacity. Microstructures of these systems are investigated by conductance, DLS, and FTIR studies. The solvation and rotational

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relaxation dynamics using picosecond time-resolved emission spectroscopy (TRES) is used to investigate the effect of $X_{Tween-85}$ as well as chemical architecture of fatty acid esters for the first time on the excited state dynamics of fluorophore. The solvation dynamics is found to be faster with an increase in $X_{Tween-85}$ and the average solvation time follows the order, EO < EP < EM, which collaborates well with droplet size and abundance of bulk-like water. Anisotropy studies reveal a decrease in the rotational restriction on the probe for EO based RMs. It is reasonable that this work have the potential to serve as good biomimicry models to study various processes occurring in biological molecules embedded in biomembranes.

1. Introduction

Surfactant molecules spontaneously accumulate in solvents to form a variety of organized assemblies such as micelle, reverse micelle (RM) or microemulsion, different lamellar phases and vesicles etc. [1]. The importance of such systems has increased substantially over years because of their various applications in many areas including drug delivery, media for membrane mimetic photochemistry and chemical reactions [2,3]. Mixtures of surfactants are often favored over the corresponding single surfactant(s) in industrial, pharmaceutical, and technological formulations for their superior performance and cost effectiveness due to their flexible physicochemical properties in terms of synergistic interaction. The quest for new and improved ionic/nonionic surfactant mixtures has now been an important topic in surface science [4–6]. As mixed micellar systems often improve therapeutic efficiency of various drugs, they find application in pharmaceutical technology [7–9]. On the other hand, aggregates of surfactants in oil continuum can solubilize substantial amount of water to form reverse micelle (RM), which emerged as a potential nano-sized system to mimic biological environment [10,11]. Doping of nonionic surfactant into the interface of ionic surfactant in RM brings about significant changes in the interfacial property as well as modifies the structure of water inside the nanopool [12–14]. Mixtures of anionic/nonionic surfactants in RM offer advantageous applications in various fields including enzyme activity, nanoparticle synthesis etc. [15,16]. In spite of extensive studies of micelles and RMs using similar set of surfactant(s) [17–20], a proper understanding at a molecular level is still in demand. In the presence study, we have investigated the effect of mixing of two surfactants (anionic and nonionic) on the physicochemical characterization of the mixed micellar solutions as well as the corresponding RMs in order to optimize and design their properties. Such investigation stands useful from both academic as well as application point of view.

We explore the micellization behavior of an anionic, sodium di-2-ethylhexylsulfosuccinate (AOT) and nonionic, polyoxyethylene (20) sorbitan trioleate (Tween-85) surfactant and their mixtures in water. Micelle formation has been investigated using extensive surface tension measurements and analysis of experimental data. AOT is a well-known biocompatible double-tailed surfactant [21], which shows unique micellization behavior compared to the single-chain conventional surfactants and has been used in lubricants and also, as emulsifiers. Microemulsion based on AOT finds application in the field of drug delivery [22–24], in which AOT increases the intestinal absorption of many drugs [25,26]. Ethoxylated nonionic Tween-85 is also biodegradable [27], making the overall formulation based on AOT and Tween-85 blends acceptable for pharmaceutical research. Here we report the micellization behavior of AOT and Tween-85 mixed systems from the viewpoint of their interfacial adsorption, nature of interaction and process energetics in detail; such study is rather sparse in the literature [28,29].

Efforts have also been made to form RMs using the combination of AOT and Tween-85 surfactants at different mixing ratios in fatty acid ethyl ester continuum, such as ethyl myristate (EM), ethyl palmitate (EP) and ethyl oleate (EO). It is important to note that apart from the difference in molar volume (Table S1, Supplementary material), these oils contain similar ethyl chain on either side of the hydrophilic ester moiety and long fatty acid chain of different lengths, viz., myristate, palmitate and oleate. Of these oils, EO contains a *cis*-double bond in the hydrocarbon chain of fatty acid (Table S1). Tween-85 RM is reported to solubilize considerable amount of water and protein [30], and possessed certain unique features for RM enzymology [31]. It was also proposed that enzymatic activities in AOT RMs are improved by the addition of nonionic surfactants into it [32,33]. Moreover, long chain fatty acid esters are environment friendly [34], low toxic and highly biodegradable [35], and most interestingly they show structural resemblance with the lipids in living systems. Also, their physicochemical behavior in surfactant/water system is much less studied than the conventional *n*-alkanes. Earlier, AOT/Tween-85 mixed RMs was successfully utilized for transdermal delivery of 5-fluorouracil, extraction of amoxicillin and topical delivery of Cyclosporin A [36–38]. But these formulated systems were mostly based on isopropyl myristate (IPM) or hydrocarbon oil. Thus, formulation and characterization of RMs stabilized in EM, EP and EO have been investigated for the first time in this report. We carry out conductivity measurement to investigate any characteristic change that occurs in the RM structure with increasing content of Tween-85 ($X_{Tween-85}$) and also, to underline the mechanism of the solubilization process. RM droplet size has been measured using dynamic light scattering (DLS) technique. The structure of the entrapped water has been determined using Fourier transform infrared spectroscopy (FTIR) measurements. The retarded dynamics of water entrapped in the mixed RMs has been studied by the solvation probe 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylamino-styryl)-4H-pyran (DCM) using picosecond resolved fluorescence spectroscopy technique. The fluorescence spectra of DCM strongly depend on the polarity of the medium [39], and hence, it can act as a good probe to contemplate the microenvironment of RMs [40,41]. The probe DCM has previously been used to report the solvation dynamics of various organized nano-assemblies [42,43]. To ascertain the geometrical restriction of the probe at the interface, rotational relaxation dynamics of DCM in these systems have also been determined. The present study thus reports micellar and reverse micellar interfacial properties of mixed surfactant systems to understand whether the key features responsible for micellization reciprocate the physical properties of water inside the RMs. The findings of this study are expected to improve the basic understanding of the formation and characterization of both mixed micellar and RM systems useful in drug delivery and as nontoxic nano-templates for future applications.

2. Experimental

2.1. Materials

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT, 99%) and polyoxyethylene (20) sorbitan trioleate (Tween-85) are purchased