

## Effect of sphere to rod transition on the probe microenvironment in sodium dodecyl sulphate micelles: A time resolved fluorescence anisotropy study

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### ARTICLE INFO

#### Article history:

Received 26 December 2008  
Received in revised form  
18 September 2009  
Accepted 17 October 2009  
Available online 25 October 2009

#### Keywords:

SDS micelle  
Hydrotropic salt effect  
Sphere to rod transition  
Coumarin-153  
Rotational relaxation  
Microviscosity

### ABSTRACT

The effect of different hydrotropic salts on the microenvironment at the anionic head group region of sodium dodecyl sulphate (SDS) micelle has been studied through time-resolved fluorescence anisotropy measurements of a solubilized probe, coumarin-153 (C153). The organic cations of the hydrotropic salts used in this study, i.e. aniline hydrochloride (AHC) and *o*-, *m*- and *p*-toluidine hydrochlorides (OTHC, MTHC and PTHC, respectively), differ in their charge to size ratio and hydrophobicity. Present study utilizes the sensitivity of the fluorescence technique to understand the changes in the micropolarity and microviscosity experienced by the fluorescent probe, C153, solubilized in the micellar Stern layer, on addition of different hydrotropic salts. Significant changes are observed in the rotational relaxation dynamics of the probe with increasing concentration of the salts. The changes in the rotational relaxation dynamics clearly reflect the sphere to rod transition in the SDS micelles and correspond nicely with the reported results from dynamic light scattering measurements. The growth behavior of SDS micelles is found to be sensitive to the hydrophobicity of the organic cations. The charge to size ratio of the organic cations also indicated to play a role in inducing the sphere to rod transition in the SDS micelles. The interesting observation made from this study is that the sphere to rod transition of SDS micelles is largely facilitated by the presence of the hydrotropic salts and such a transition is successfully indicated by the simple fluorescence anisotropy measurements of a probe in the micelle carried out in the presence of different hydrotropic salts.

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### 1. Introduction

Understanding the structure of micelles under various physicochemical conditions has found immense research interest due to the applications of such systems in industries to modify the mechanism and dynamics of chemical reactions [1–3] and designing drug carrier and delivery systems [4]. Micelles are known to exist in varying sizes, shapes and compositions depending upon the salt conditions, temperature, pH and composition of the solution. Micelles are found as an approximate model for drug and DNA delivery vehicles, and also to mimic many characteristics of biological bilayer membranes [5]. Thus, understanding the possibility of tuning the structures and hence the properties of micelles, is always worthwhile to investigate thoroughly. Apart from the micellar structure and properties, other important constituent that plays crucial role in influencing micro-reactions happening inside the micellar environment is its confined water. The confined water present inside the micelles is of two kinds, namely the thermodynamically bound (hydrogen bonded to surfactant chains) water and

the mechanically trapped water [6–8]. The properties of confined water, such as viscosity, polarity, mobility, etc. are very different from that of bulk water due to their confinement, specific interactions and presence of microenvironment containing ions or salts [9,10]. Thus, understanding the extent of hydration of micellar Stern layer and the dynamics of the confined water is very important for complete understanding of the micelles [5,10–12].

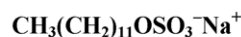
It is well established that the counterions have a strong influence on the critical micelle concentration (CMC), aggregation number, size and shape of the micellar aggregates of ionic surfactants [13–15]. The micelles change their shapes on addition of co-surfactants [16], inorganic salts [17], or strongly binding organic salts [18]. Addition of inorganic salts like alkali metal salts (LiCl, NaCl, KCl and CsCl) increases the size and hydration of micelles as it increases the ionic strength of the medium and thus decreases the effective repulsive interactions between head groups of the surfactant molecules [19–22]. However, a reasonably large amount of an inorganic salt is required to appreciably increase the shape and size of the micelles [23,24], whereas organic salts having aromatic counterions often induce the formation of rod-like micelles at relatively low surfactant and counterion concentrations [25,26]. Organic salts with a hydrophobic part in the counterion have the greater ability to penetrate the head group region of the micellar Stern layer

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and thus effectively neutralize the surface charges. Hence, the electrostatic repulsion between the ionic hydrophilic groups of the surfactants decreases along with a simultaneous increase in the hydrophobic interactions in the Stern layer of the micelles, leading to the tighter packing of the surfactant-counterion mixed systems facilitating more aggregation of the surfactant molecules. It is well known that small amounts of sodium salts of aromatic counterions like salicylates [27,28], *p*-toluenesulfonate [29], chlorobenzoates [30] and naphthalene carboxylates [31,32], etc. are very effective in inducing the uniaxial growth of globular ionic micelles into the worm-like micelles [33]. The sphere to rod transitions in micelles changes the viscoelastic and rheological properties of the solutions [31,34]. The systems containing worm-like micelles are discussed intensely as drug reducing agents (DRA) in recirculation systems [35,36], fracturing fluids in oil production [37] and many home and personal care products [38]. The effect of addition of aniline hydrochloride (AHC) salt on the size and shape of SDS micelles and thus the effect of micellar size variations on the polymerization of aniline inside the micelles during shape transitions have been investigated recently by dynamic light scattering (DLS) measurements [39]. Although these shape transitions are extensively studied in cationic surfactants, there are relatively limited reports on wormlike micelles of anionic surfactants.

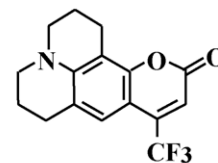
Recently Hassan et al. [40] and Garg et al. [41] have presented the DLS and small angle neutron scattering (SANS) studies to emphasize the role of hydrotropic salts like toluidine hydrochlorides in converting the spherical sodium dodecyl sulphate (SDS) micelles into rod-like micelles at a reasonably low salt to surfactant ratio. The experimental techniques like DLS and SANS have been very effective in determining the size, shape, effective head group area, etc. of SDS micelles in the presence of varying amounts of hydrotropic salts [40–42]. It has been established that the hydrophobicity and the orientation of the aromatic rings of the organic counterions have significant influence on the extent of interaction and the micellar growth [40–42]. The DLS, SANS, and NMR techniques have been able to differentiate the influence of aniline hydrochloride (AHC), and *o*-, *m*-, *p*-substituted toluidine hydrochloride (OTHC, MTHC and PTHC respectively) on physical characteristics of SDS micelles [40,41]. The NMR measurements have shown the presence of PTH<sup>+</sup> ion (cation of PTHC salt) inside the Stern layer of SDS micelles [42]. The axial growth behavior of micelles is found to be faster with PTHC and MTHC than AHC and OTHC. The reason for this difference has been attributed to the fact that the presence of methyl groups at *p*- and *m*-positions facilitates the penetration of PTH<sup>+</sup> and MTH<sup>+</sup> cations deeper inside the Stern layer, leading to a better charge neutralization of the micellar surface charge density. Apart from these gross physical characterizations, there have been no studies in the literature, to understand the changes in the microenvironments of the micellar Stern layer during the sphere to rod shape transitions. The question remains whether the overcrowding of the head groups during the sphere to rod transition results in a reduction in the hydration of the Stern layer, whether the microviscosity of the Stern layer increases or decreases during such transitions, etc.? Time-resolved fluorescence techniques have been well suited to probe the micellar interiors using appropriate fluorescent probe that solubilizes conveniently at the site of interest in the micellar microstructure. The selectivity and sensitivity of the fluorescence technique has been sufficient enough to indicate the small variations in the structures and the hydration characteristics of the Stern layers of micelles, vesicles and even the dynamics of the confined water around proteins and DNA strands [12]. To the best of our knowledge the fluorescence technique has not been used to probe the changes in the microenvironment in the Stern layer of SDS micelles during the sphere to rod transitions of these micelles in the presence of hydrotropic salts.

## Surfactant



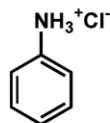
Sodium dodecyl sulphate  
(SDS)

## Probe Dye

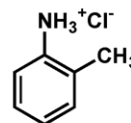


(C153)

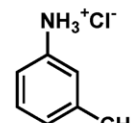
## Hydrotropic Salts



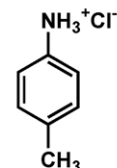
Aniline  
hydrochloride  
(AHC)



*o*-Toluidine  
hydrochloride  
(OTHC)



*m*-Toluidine  
hydrochloride  
(MTHC)



*p*-Toluidine  
hydrochloride  
(PTHC)

**Chart 1.** The molecular formula of SDS and the chemical structures of C153 dye and the different aromatic salts used in this work are shown.

In this work we present the time-resolved fluorescence anisotropy study to understand the changes in the micropolarity and microviscosity of the Stern layer of SDS micelles during sphere to rod transition in the presence of hydrotropic salts using coumarin-153 (C153) as the fluorescent probe. The probe is established to preferably reside in the Stern layer (head group region) of the micelles mainly due to the dipolar character of the dye [19–21]. Hydrotropic salts like AHC, OTHC, MTHC and PTHC have been used to induce the shape transitions in the SDS micelles [40,41]. Present work focuses on the understanding of the changes in the microviscosity and the hydration characteristic of the Stern layer of the SDS micelles due to the interplay of the hydrophobicity and the charge to size ratio of the hydrotropic salts, as revealed by the rotational relaxation dynamics studies of the fluorescent probe.

## 2. Experimental

SDS surfactant (>99% purity) was obtained from Sigma, USA. Laser grade C153 was obtained from Exciton, USA. The salts AHC and PTHC were obtained from Fluka and OTHC was obtained from Aldrich. MTHC was prepared using the procedure described earlier [41]. The molecular formula of SDS and the chemical structures of C153 dye and different aromatic salts used in this work are shown in Chart 1.

In the present study the C153 concentrations were kept  $\sim 10 \mu\text{M}$  and the surfactant concentrations were kept  $\sim 50 \text{mM}$  in all the cases. The solutions were prepared using nanopure water obtained from Millipore Elix-3/A10 system. Concentration of the hydrotropic salts were varied from 4 mM to 35 mM (salt-to-surfactant ratio,  $x_{\text{salt}} = [\text{salt}]/[\text{surfactant}]$  varying from 0.08 to 0.7) keeping the surfactant concentration same ( $[\text{SDS}] \sim 50 \text{mM}$ ).

Steady-state (SS) fluorescence spectra were recorded using Hitachi F-4010 spectrofluorimeter. Time-resolved fluorescence measurements were carried out using a diode-laser-based time-correlated single-photon-counting (TCSPC) spectrometer [43] from IBH, U.K. Briefly, a 374 nm diode laser (1 MHz) was used to excite the sample and a microchannel plate-photomultiplier tube (MCP-PMT) was used to detect the fluorescence photons from the sample. The instrument response function was measured to be  $\sim 100 \text{ps}$

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