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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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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.

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 cosurfactants [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^+ 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^+ and MTH^+ 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.

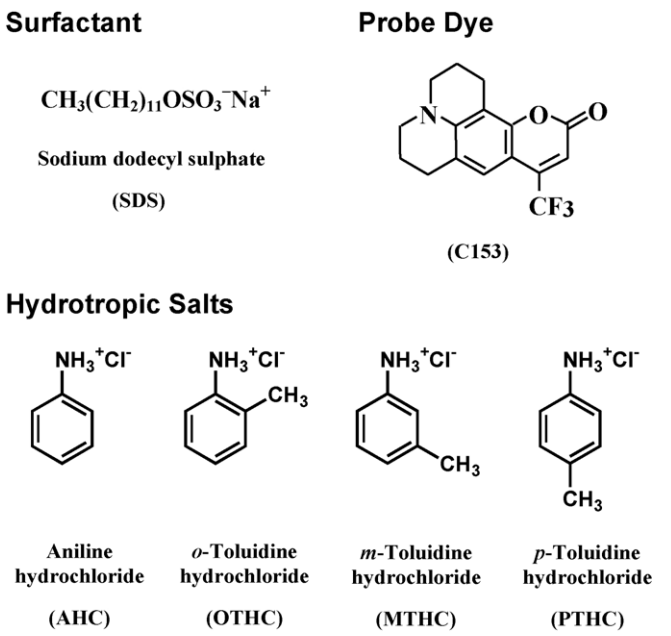

Chart 1. The molecular formula of SDS and the chemical structures of C153 dye and the different aromatic salts used in this work are shown.

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 ~10 μM and the surfactant concentrations were kept ~50 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_{salt} = [salt]/[surfactant] varying from 0.08 to 0.7) keeping the surfactant concentration same ([SDS] ~50 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 ~100 ps

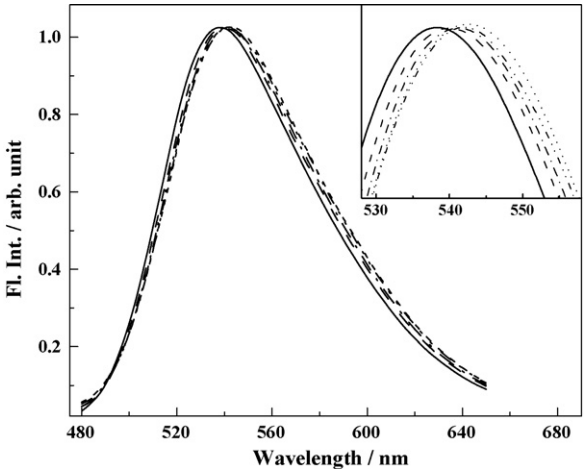

Fig. 1. Normalized fluorescence spectra of C153 dye in SDS micelle in the absence (solid line) and in the presence of 10 mM (dashed line), 15 mM (dash dotted line), 25 mM (dash double dotted line) and 35 mM (short dashed line) concentrations of OTHC salt. Inset: expanded plot for the peak region of the spectra, showing a clear red shift in the peak position with the increasing salt concentration. The trends were very similar in the presence of the other hydrotropic salts used in this study.

at full-width-half-maximum (FWHM). All the measurements were carried out at room temperature (298 ± 1 K) and the temperature was controlled using a microprocessor based temperature controller (model DS from IBH) in combination with a heating and cold-finger arrangement. Fluorescence decays, $I_{||}(t)$ and $I_{\perp}(t)$, with polarizations parallel and perpendicular to the vertically polarized excitation beam, respectively, were measured and anisotropy decay functions $r(t)$ were constructed using the following relation [43]:

$$r(t) = \frac{I_{||}(t) - GI_{\perp}(t)}{I_{||}(t) + 2GI_{\perp}(t)} \quad (1)$$

where G is a correction factor for the polarization bias of the detection system and was estimated independently following the standard procedure [43]. Measurements were repeated for 3 times to check the reproducibility and to obtain the average values of the measured relaxation times.

3. Results and discussion

Fluorescence emission spectra of C153 were recorded in SDS micelles with and without the addition of the hydrotropic salts (AHC, OTHC, MTHC and PTHC). The emission spectra show a small red shift with the addition of the salts as shown in Fig. 1 for the typical case of OTHC, the trend being similar for the other salts. In fact, with the highest salt concentrations used, the normalized fluorescence spectra of the dye in the presence of all the four salts used were almost indistinguishable and hence not shown in the figure. It has already been established in earlier studies that the probe C153 resides in the Stern layer of the micelles [20,21]. Thus, the red shift in the fluorescence maxima (~6 nm in the presence of ~35 mM of hydrotropic salts) suggests that the micropolarity around the probe

Table 1
Fluorescence lifetimes and rotational correlation times along with their relative contributions for C153 dye in SDS micelle at varying concentrations of the hydrotropic salts.

Conc.	τ_f/ns[a]	a_{r1}	τ_{r1}/ns[a]	a_{r2}	τ_{r2}/ns[a]	$\langle\tau_r\rangle$/ns[a]	$\langle\tau_r\rangle/\langle\tau_0\rangle$
0 mM	3.81	0.08	0.10	0.92	0.68	0.62	1.0
AHC							
4 mM	3.51	0.16	0.13	0.84	0.76	0.66	1.06
8 mM	3.42	0.11	0.16	0.89	0.71	0.65	1.05
12 mM	3.39	0.13	0.14	0.87	0.74	0.66	1.06
16 mM	3.35	0.16	0.17	0.85	0.74	0.65	1.05
20 mM	3.32	0.18	0.20	0.82	0.90	0.77	1.24
25 mM	3.30	0.13	0.15	0.87	0.89	0.79	1.27
30 mM	3.23	0.11	0.15	0.89	0.91	0.83	1.33
35 mM	3.21	0.19	0.18	0.81	1.03	0.87	1.40
OTHC							
4 mM	3.27	0.19	0.15	0.80	0.78	0.65	1.05
8 mM	3.20	0.27	0.19	0.73	0.85	0.67	1.08
12 mM	3.16	0.20	0.14	0.80	0.82	0.68	1.10
16 mM	3.12	0.22	0.16	0.78	0.85	0.70	1.13
20 mM	3.10	0.30	0.24	0.70	1.18	0.90	1.45
25 mM	3.06	0.16	0.15	0.84	1.04	0.90	1.45
30 mM	3.02	0.25	0.28	0.75	1.14	0.93	1.50
35 mM	2.98	0.23	0.21	0.77	1.20	0.97	1.56
MTHC							
4 mM	3.25	0.24	0.16	0.76	0.82	0.66	1.06
8 mM	3.15	0.22	0.14	0.78	0.83	0.68	1.10
12 mM	3.10	0.25	0.16	0.76	0.85	0.68	1.10
16 mM	3.05	0.34	0.22	0.66	1.23	0.89	1.43
20 mM	3.01	0.31	0.23	0.69	1.22	0.91	1.47
25 mM	2.93	0.25	0.22	0.75	1.23	0.98	1.58
30 mM	2.86	0.39	0.30	0.61	1.58	1.08	1.74
35 mM	2.82	0.33	0.27	0.67	1.44	1.05	1.69
PTHC							
4 mM	3.35	0.11	0.12	0.89	0.68	0.62	1.00
8 mM	3.25	0.12	0.14	0.88	0.74	0.67	1.08
12 mM	3.19	0.10	0.12	0.90	0.69	0.64	1.03
16 mM	3.15	0.28	0.25	0.72	1.04	0.82	1.32
20 mM	3.13	0.27	0.25	0.73	1.07	0.85	1.37
25 mM	3.12	0.18	0.23	0.82	1.06	0.91	1.47
30 mM	3.05	0.21	0.28	0.79	1.21	1.01	1.64
35 mM	3.00	0.22	0.30	0.78	1.18	0.98	1.59

[a] The error limits in the τ_f, τ_{r1}, τ_{r2} and $\langle\tau_r\rangle$ values are about 2%, 15%, 6%, and 7% respectively.

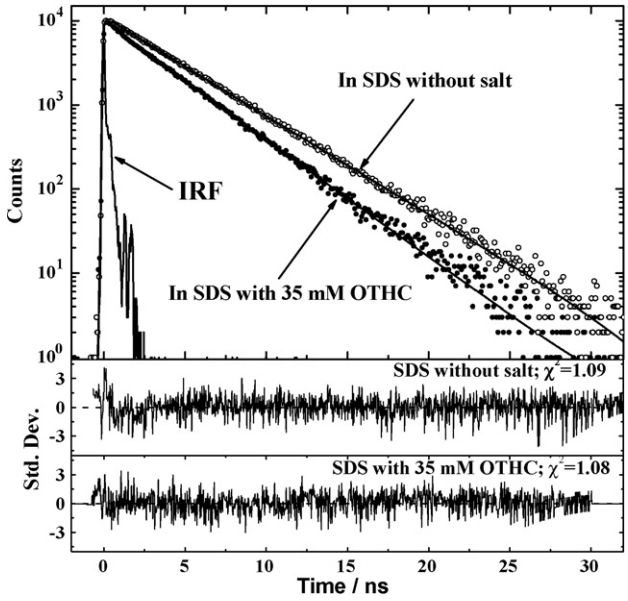

Fig. 2. Fluorescence decay curves and their single-exponential fits for C153 dye in SDS micelle in the absence of any salt and in the presence of 35 mM of OTHC as indicated in the figure. The lifetime values are listed in Table 1. The distribution of the weighted residuals for the above fits among the data channels and the respective χ^2 values are given in the lower panel of the figure.

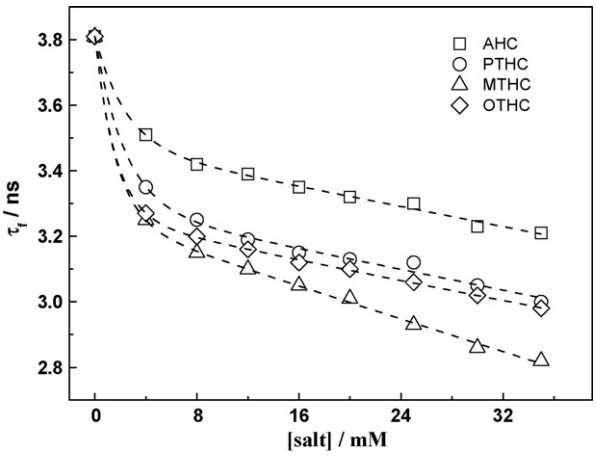

Fig. 3. Fluorescence lifetime values of C153 as a function of the concentration of different hydrotropic salts in SDS micellar solution.

in the Stern layer increases to some extent on the addition of the hydrotropic salts. Present observation is thus in accordance with the literature reports suggesting an increase in the size and hydration of the micelles with the addition of the salts in the micellar solution [20,21]. In few of the earlier studies where the probe C153 was used in neutral micelles (TX-100) to understand the influence of inorganic salts (LiCl, NaCl, KCl and CsCl) on the structure and hydration of the micellar Stern layer, no shift in the fluorescence spectra were observed [44,45]. The observation was rationalized by the movement of the probe molecule deeper inside the micellar Palisade layer to compensate the increased micropolarity due to the increased hydration at the head group region. In the present case, since the width of the Stern layer of the anionic SDS micelle is not large enough (i.e. about 9 Å [46], just comparable to the diameter of the probe C153), there is not much of scope for the probe to move deeper inside the Stern layer to counterbalance the increased polarity due to the addition of the salts in the solution. Accordingly, the fluorescence spectra of C153 show a small red shift in the presence of the added hydrotropic salts, indicating a small increase in the polarity around the probe in the Stern layer of SDS micelles.

We carried out fluorescence lifetime and fluorescence anisotropy measurements of the probe C153 in SDS micelles, to monitor the changes in the microenvironment occurring inside the Stern layers during the sphere to rod transitions. We also tried to see if the differences in the hydrophobic character of the salts have some effect in inducing the structural changes in the micelles. There is also an interest to see whether the method is sensitive enough to indicate the sphere to rod transition of the micelles, which is of utmost importance to understand these micro-heterogeneous systems. For fluorescence lifetime and fluorescence anisotropy measurements, the probe C153 was added to the solution of 50 mM SDS micelles having varying concentrations of AHC, MTHC, OTHC and PTHC. Table 1 shows the fluorescence lifetime (τ_f) values of the probe as measured at the emission maxima in the respective cases with varying concentrations of the hydrotropic salts in the SDS solution. It is to be mentioned that in all these cases the fluorescence decays of the dye fitted nicely with a single-exponential function, as also reported in the earlier studies for the dye in SDS micelle [21]. Fig. 2 presents two typical fluorescence decays of C153 dye in SDS micelle in the absence of any salt and in the presence of 35 mM of OTHC along with their single-exponential analysis, as the representative of the present systems. The single-exponential nature of the fluorescence decays suggest that the dye molecules are solubilized in the more or less similar locations in the SDS micelles. As inferred in our earlier study, the coumarin dyes are mainly solubilized in the Stern layer of the SDS micelles [21]. Since the thickness of the Stern layer of SDS micelles is not that large (~9 Å [46]), it is expected that the dye molecules in SDS micelles do not have any wide distribution for their solubilization sites. The changes in the τ_f values with the salt concentration are plotted in Fig. 3. As indicated from Table 1 and Fig. 3, the fluorescence lifetime of the probe residing inside the Stern layer of the SDS micelle decreases gradually with an increase in the salt concentration. It is possible that the decrease in the fluorescence lifetime on the addition of the salts is due to an increase in the hydration of the Stern layer, causing an enhancement in the nonradiative decay rate of the excited probe.

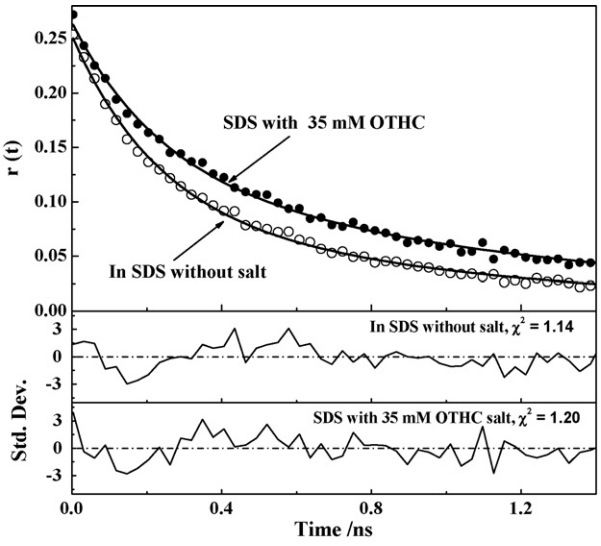

Fig. 4. Fluorescence anisotropy decays and their bi-exponential fits for C153 dye in SDS micelle in the absence of any salt and in the presence of 35 mM of OTHC as indicated in the figure. The rotational correlation times and their relative amplitudes are listed in Table 1. The distribution of the weighted residuals for the above fits among the data channels and the respective χ^2 values are given in the lower panel of the figure.

It may as well be due to an increase in the number of the surfactant head groups in the Stern layer (as indicated from the increase in the rotational relaxation times, discussed later) that can lead to an increase in the nonradiative decay rate due to the increased ion–dipole interaction, resulting in a decrease in the fluorescence lifetime of the probe.

The anisotropy decay of the probe was found to be bi-exponential in nature for all the cases studied. Typical fluorescence anisotropy decays of C153 dye in SDS micelle in the absence of any salt and in the presence of 35 mM of OTHC along with their bi-exponential analysis are shown Fig. 4 as the representative decays for the present systems. Table 1 shows the list of the two anisotropy decay time constants (τ_{r1} and τ_{r2}, respectively) along with their relative amplitudes (a_{r1} and a_{r2}, respectively) as obtained in the presence of different salts with their varying concentrations in the SDS micellar solution. The average rotational relaxation time $\langle\tau_r\rangle$, as calculated using the following relation:

$$\langle\tau_r\rangle = a_{r1}\tau_{r1} + a_{r2}\tau_{r2}, \quad (2)$$

where τ_{r1} and τ_{r2} are the fast and slow rotational correlation times and a_{r1} and a_{r2} are their relative amplitudes, respectively, are also listed in Table 1. As indicated from Table 1, though there is a relatively higher scatter in the τ_{r1} values, yet all the τ_{r1}, τ_{r2} and $\langle\tau_r\rangle$ values effectively show an increasing trend with an increase in the salt concentration in the solution.

For the bi-exponential anisotropy decays, as observed for the present systems, one of the possibilities could be that the probe resides in two different solubilization sites in the micelle of having largely different microenvironments and thus the probes at the two sites experiences two different rotational relaxation dynamics. Such a situation is, however, not supported by the observation that the fluorescence decays of the probe in SDS micelle show a single-exponential behavior for all the salt concentrations used. That the probe C153 solubilizes preferentially in the micellar Stern layer [21], and that the Stern layer thickness for SDS micelle is similar to that of the probe dimension [46] also suggest that in the present cases the dye molecules are solubilized more or less in the similar location of the SDS micelles without much of variations in their microenvironments. The other possibility that the viscous microenvironment for the dye in the micellar Stern layer can simply be a reason for the bi-exponential anisotropy decay is also not supported by the fact that in a viscous but homogeneous solution like that in ethylene glycol ($\eta \sim 17.3$ cP), the anisotropy decay of C153 dye follows a clear single-exponential behavior [47] with a rotational time constant of about 240 ps, significantly lower than the τ_{r2} value observed in the present cases. Thus, excluding the above two possibilities, the bi-exponential anisotropy decays for the dye in the micellar Stern layer can be rationalized by considering the effects of different kinds of rotational motions possible for the probe and the micelle. As evident, for such systems, three kinds of rotational motions can contribute to the anisotropy decay of the probe, and they are the wobbling motion of the probe at the micellar Stern layer, lateral diffusion of the probe along the Stern layer of the micelle and the direct overall rotation of the whole micelle [48,49]. Considering the interplay of the above three motions on the fluorescence depolarization of the probe, as are incorporated in the well-known two-step model [48,49], the anisotropy decay of the probe solubilized in the micellar Stern layer is suggested to follow a clear bi-exponential behavior. Since the size of the micelle is in general quite large to make the rotation of the whole micelle very slow (time constants of tens of nanosecond) as compared to the wobbling motion (time constants of fraction of nanosecond) and the lateral diffusion (time constants of few nanoseconds) of the probe [48,49], the contribution of the whole micelle rotation on the observed fluorescence depolarization dynamics (occurs with time constants of fraction of a nanosecond to few nanoseconds) of the probe is usually very negligible [47–49]. Further, the largely different times scales for the wobbling motion and lateral diffusion of the probe suggest that the experimentally observed rotational correlation times, τ_{r1} and τ_{r2} can approximately be correlated with the wobbling motion (fast component) and lateral diffusion (slow component) of the probe, respectively [47–49]. As both the wobbling motion and the lateral diffusion of the probe is strongly dependent on the microviscosity at the micellar Stern layer, it is expected that the changes in the τ_{r1}, τ_{r2} and $\langle\tau_r\rangle$ values will report the changes in the microviscosity around the probe molecule in the micellar Stern layer due to the addition of the salts in the present systems.

As seen from Table 1, the τ_{r1} value of the probe (corresponding to the wobbling motion) apparently increases on increasing the salt concentration in the SDS micellar solution, though the data shows quite large fluctuations mainly because of the fact that the τ_{r1} values are almost in the range of the instrument response function for the present experimental setup (IRF $\sim$ 100 ps at FWHM). Thus, a systematic correlation between the τ_{r1} values and the salt concentrations was not possible to obtain. The τ_{r2} value of the probe in the micelle, however, shows a more systematic increase with the increasing concentration of the salts, though the changes in its relative contribution a_{r2} are not that systematic. This indicates the inherent problem in the data recovery following the bi-exponential analysis of the anisotropy decays, especially because the variations in the τ_{r1} and τ_{r2} values are almost in the range of the IRF of the present experimental setup. In the present study, since our main interest is to know the effective changes in the anisotropy decay dynamics, we thus mainly considered the changes in the $\langle\tau_r\rangle$ values of the probe with the varying salt concentrations, because the $\langle\tau_r\rangle$ values is expected to give us the average effect of the changes in the individual rotational relaxation times and their relative amplitudes caused by the presence of the salts in SDS micellar solution. As are seen from Table 1, the $\langle\tau_r\rangle$ value increases systematically on increasing the salt concentration in the system. The rise in the $\langle\tau_r\rangle$ value suggests an increase in the microviscosity around the probe in the micellar Stern layer with the addition of the salts used. Fig. 5 shows the plot of the ratio, $\langle\tau_r\rangle/\langle\tau_0\rangle$, as a function of concentration of the different salts used, where $\langle\tau_r\rangle$ represents the average rotational relaxation time of the probe in presence of the salt and $\langle\tau_0\rangle$ corresponds to the probe relaxation time in the absence of the salt.

As indicated from Fig. 5, for all the hydrotropic salts used, the $\langle\tau_r\rangle/\langle\tau_0\rangle$ ratio increases with an increase in the salt concentration. The best possible correlation that can be considered for the changes in the $\langle\tau_r\rangle/\langle\tau_0\rangle$ ratio with the concentration of the salts is appeared to be sigmoid in nature. Thus, the initial changes in the $\langle\tau_r\rangle/\langle\tau_0\rangle$ ratio with the salt concentration is not that significant but it undergoes a reasonably sharp change at an intermediate salt concentration and there after the changes are again not that large at the higher salt concentrations. It is evident from the sharp inflection in the plots of the $\langle\tau_r\rangle/\langle\tau_0\rangle$ values versus the salt concentrations that there is a sudden change/increase in the microviscosity in the Stern layer at the region of the salt concentrations that correspond to these changes. We presume that this is due to a sudden enhancement in the crowding of the surfactant head groups in the micelles caused by the presence of these optimum salt concentrations resulting a kind of excess growth or major structural change in the micelles. In correlating the nature of variations in the $\langle\tau_r\rangle/\langle\tau_0\rangle$ values with the changes in the micellar microenvironment, we suggest from the observed results that the microviscosity around the probe remains more or less similar at the lower salt concentrations but there is a sharp increase in the microviscosity for the salt concentration range of $\sim$12–24 mM depending on the nature of the hydrotropic salt used. It is worth mentioning at this point that the observed microviscosity changes inside the micellar environment corroborate well with the macroscopic micellar growth as suggested in some of the earlier reports from DLS and SANS measurements [40,41].

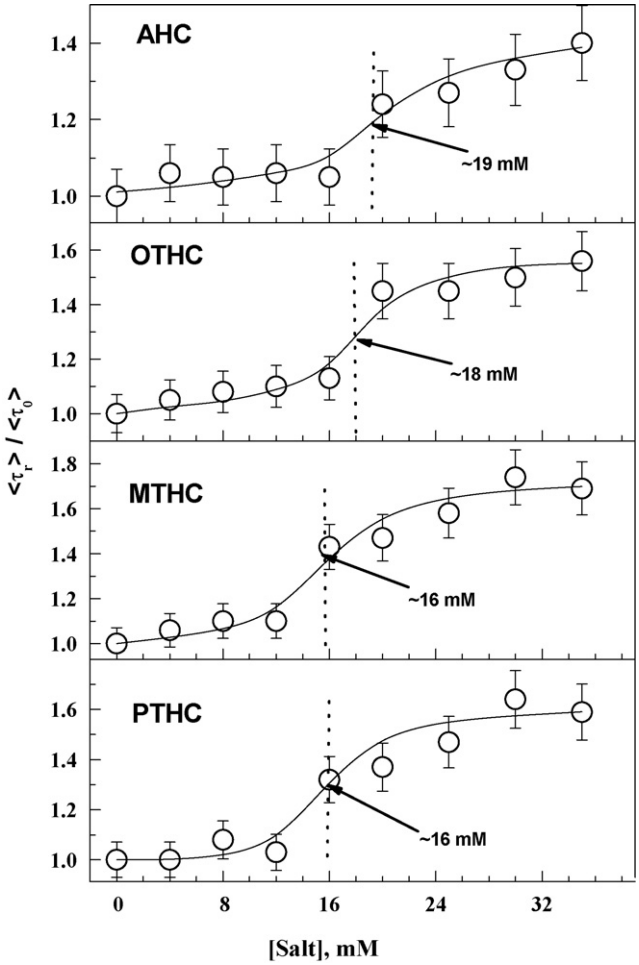

Fig. 5. The variations in the $\langle\tau_r\rangle/\langle\tau_0\rangle$ ratio for C153 dye in SDS micellar solution as a function of the concentration of different hydrotropic salts used. In all the cases there is a clear inflection in the plots at an intermediate salt concentration, indicating the sphere to rod transition in the micelles.

As realized from the literature reports, in the presence of the hydrotropic salts, the growth of micelles is not at all symmetric but the micelles mainly grow in one direction, changing the shape of the micelles from spheres to rods [40,41]. Furthermore, it is indicated that the longitudinal growth of the micelles is initially slow at the lower salt concentrations, and only after a certain optimum concentration of the salt used the growth enhances drastically, causing a sharp change in the micellar shape. It is suggested in the literature that with an increase in the amount of salt in the micellar solution the effective size of the head group area per surfactant decreases in the micelles, causing a crowding of the surfactant head groups, which eventually leads to the stretching in the micellar structure, resulting in the transformation of the spherical micelles to the rod-shaped micelles as the salt concentration is made beyond an optimum value [40,41]. It is realized that such a growth of a micelle is greatly assisted by the absorption of the aromatic counterions on the oppositely charged surface of the micelles, causing neutralization of the surface charges thus reducing repulsions among the adjacent head groups. We suppose that such a sphere to rod transition in the micelle is the cause for the observed inflection in the $\langle\tau_r\rangle/\langle\tau_0\rangle$ versus salt concentration plots as observed in the present study at an intermediate salt concentrations of ~12–24 mM depending on the nature of the hydrotropic salt used.

Present observation suggests that the transition of the micelles from the sphere to the rod-like shape possibly occurs in the concentration range of 12–24 mM for all the salts. A close look into the plots in Fig. 3 suggests that the growth behavior of the SDS micelles is apparently different with different hydrotropic salts (AHC, MTHC, OTHC and PTHC) used, which is also expected to be complemented by the microviscosity changes occurring inside the SDS micelles in the presence of these salts. Interestingly, the changes in the $\langle\tau_r\rangle$ values in the presence of MTHC and PTHC salts are somewhat different than that observed with AHC and OTHC salts. Fig. 5 effectively shows that in case of MTHC and PTHC the onset of the sphere to rod transition probably starts at a relatively lower salt concentrations (inflection occurs at ~16 mM), than AHC and OTHC salts (inflection occurs at ~19 mM). Furthermore, the increase in the average relaxation time of the probe inside the micelles is observed to be relatively more with MTHC and PTHC salts than with AHC and OTHC salts at the higher salt concentrations (~30 mM). We feel that these differences are related to the charge to size ratio and/or to the hydrophobicity of the organic cations of the hydrotropic salts, as these parameters are expected to play a crucial role in determining their penetration into the micelles and thus influencing the shape change in micellar structure. The charge to size ratio of AHC is the largest among all the salts used in this study and thus a small quantity of AHC can cause significant reduction in the repulsions among the SDS head groups. In case of OTHC, MTHC and PTHC, though all of them have quite similar charge to size ratio but their hydrophobicity should be significantly higher (due to the presence of the additional methyl substituent in the aromatic ring) than AHC. Thus, OTHC, MTHC and PTHC should have a higher tendency to penetrate deeper inside the Stern layer and thus to give better effect on the micellar growth than AHC. This is in fact evident from Fig. 5, indicating that the effective micellar growth even at the higher concentration range of salts used is the minimum for AHC compared to the other three toluidine hydrochloride salts used in the present study. In this respect, however, OTHC shows somewhat exceptional results than MTHC and PTHC, which is possibly due to the presence of the methyl group at the *o*-position of the phenyl ring that makes the organic cation relatively less hydrophobic compared to MTHC and PTHC. The reason for the strongest effect with MTHC in inducing the sphere to rod transition is attributed to the presence of hydrophobic methyl group at the *m*-position which possibly facilitates a better penetration and anchoring of the aromatic ring to the micellar Stern layer, neutralizing the head group charges more effectively and thus causing larger rod-shaped micelles to be formed. For PTHC with its methyl group at the *p*-position, it is likely that the aromatic ring undergoes quite similar penetration in the Stern layer as that of MTHC and thus causes a reasonably stronger effect on the micellar growth behavior.

The observed increase in the $\langle\tau_r\rangle$ values and accordingly an increase in the microviscosity in the Stern layer of the micelles apparently contradicts with the expected increase in the polarity or hydration of the micellar Stern layer with the addition of the salts, as indicated from the red shifts in the fluorescence spectra of the probe and is also reported in the literature [40,41]. Increased polarity of the Stern layer means that the water content in the Stern layer increases with the addition of the aromatic salts in the solution. Thus, under normal circumstances it was expected that the increased hydration with the added salt would cause a decrease in the microviscosity inside the Stern layer and consequently a decrease in the rotational time of the probe. It has to be mentioned here that at the lower salt concentration region there is no large variation in the $\langle\tau_r\rangle/\langle\tau_0\rangle$ ratio values as observed in the present study (*cf.* Fig. 5) though the DLS and SANS measurements [40,41] reported some increase in the aggregation number of the micelles at the low salt concentration region also. It can be justified that at the lower salt concentrations there is a counterbalance between the increase in the microviscosity due to the increase in the sur-

factant packing fraction and the decrease in microviscosity due to the increase in the hydration of the Stern layer, causing the fluorescence anisotropy decay dynamics of the probe not that sensitive to the salt concentration. However, the effect of the micellar growth apparently dominates over the effect of increased hydration as the sphere to rod transition is set in at some optimum salt concentration and thus at these salt concentrations there is a large increase in the rotational relaxation times ($\langle\tau_r\rangle$) for the probe. From the present results, it is indicated that even though there is an increase in the hydration of the Stern layer, the overall longitudinal growth of the micelle and the consequent overcrowding of the surfactant head groups in the Stern layer mainly influences the rotational behavior of the probe in the presence of the added hydrotropic salts. It may also be inferred that in contrary to the general effect of the added inorganic salts that increases the hydration of the micelles very largely, the aromatic salts have a tendency to increase the surfactant population more in the micelle than the surge of the water molecules inside the Stern layer. Thus, the effect of aromatic salts to the micellar structure is significantly different from that of the inorganic salts, in which case the growth of the micelle is slow and accordingly the relative increase in the hydration is much higher. Unlike this, in the case of aromatic salts, the increase in the micellar size is relatively more prominent than the increase in the micellar hydration. In other words, the presence of organic salts causes a overcrowding of the surfactant head groups in the Stern layer which does not allow a large uptake of water inside the Stern layer as in the case of an inorganic salt. Accordingly, the probe experiences much higher microviscosity inside the Stern layer of the micelles (due to the crowding of surfactant head groups) in the presence of the aromatic salts. With this understanding we can thus expect that the decrease in the fluorescence lifetime of the probe with the addition of the organic salts in the SDS micellar solution would mainly be due to the effect of the crowding of the surfactant head groups and the consequent ion–dipole interactions rather than the effect of the increased hydration of the Stern layer to enhance the nonradiative deexcitation rate for the excited dye in the micelle.

The present study relating the characteristics of the hydrotropic salts in inducing the different growth behavior in a micelle have a potential scope in tuning the physico-chemical properties of the micelles. The Stern layer is considered as an important part of a micelle as it provides a range of restricted environments (having a range of microviscosity and hydration along with a small range of distance), which poses an ideal environment for solubilization of different solutes to perform various reactions under confinement. Such systems can also be used as the transport vehicles for different molecules. The exact nature of the microenvironments inside the Stern layers is difficult to understand as it has mixed contributions from surfactant head groups, their hydrophobic chains, and also from trapped water molecules, etc. The fluorescence probe that preferentially locates itself inside the micellar Stern layer is quite often utilized to monitor the variations in the microenvironments of the Stern layer. In this study we have successfully utilized the fluorescence technique to probe the changes occurring inside the Stern layer of SDS micelle during the micellar shape transitions in the presence of the hydrotropic salts. We are able to demonstrate that the overcrowding of the surfactant head groups in the presence of the hydrotropic salts mainly influence the growth of the micelle and this effect dominates over the increase in the hydration of the Stern layers in the presence of these salts. It is inferred from the present study that the organic salts with higher hydrophobicity are more effective in inducing the sphere to rod transition of micelles compared to the hydrophilic inorganic salts. Further insights about the tunability of microenvironments inside the micelles would be our next step in the process of having better understanding of these systems.

4. Conclusions

In this work we present the time-resolved fluorescence anisotropy measurements of the probe C153 located inside the Stern layer of SDS micelles to monitor the changes occurring around its microenvironment during the sphere to rod micellar shape transition brought about by the addition of the hydrotropic salts. The hydrotropic salts differ with the presence of methyl group at different positions of the aromatic ring and thus vary in their charge to size ratio and also in their hydrophobicity. The observed variations in the fluorescence lifetimes and time-resolved fluorescence anisotropy with different salts follow the same trends, which are in accordance with the reported results in the literature from DLS and SANS studies. Present results indicate that unlike the inorganic salts, the organic salts cause the growth of the micelle to be more prominent than the increase of the micellar hydration. In the present study, the variations in microenvironment of the Stern layer have been characterized by the relatively simple rotational dynamics measurements of a fluorescence probe, which is quite successful in detecting the sphere to rod transition of SDS micelles. The study enhances the understanding of the micellar growth behavior in the presence of different kinds of aromatic salts of varying hydrophobicity and suggests a possibility of tuning the properties (surface active behavior, viscosity, geometry, polarity, etc.) of the micelles by the use of a suitably chosen organic salt.

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