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# Micellar dipole potential is sensitive to sphere-to-rod transition

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#### ABSTRACT

Structural transitions involving shape changes play an important role in cellular physiology. Charged micelles offer a convenient model system in which structural transitions can be suitably induced by increasing the ionic strength of the medium. In this paper, we have explored sphere-to-rod transition in charged micelles of SDS and CTAB by monitoring micellar dipole potential using the dual wavelength ratiometric approach utilizing the potential-sensitive membrane probe di-8-ANEPPS. Our results show that micellar dipole potential is sensitive to sphere-to-rod transition in charged micelles. Micellar dipole potential exhibited increase with increasing ionic strength (salt), irrespective of the nature of micellar charge, implying considerable dipolar reorganization underlying structural transitions. We interpret the increase in dipole potential due to sphere-to-rod transition because of an increase in the population of confined (norrandom) dipoles induced by micellar organizational change. This is due to the fact that dipole potential arises due to the *nonrandom* arrangement of micellar dipoles and water molecules at the micelle interface. Our results constitute one of the first reports describing drastic dipolar reorganization due to micellar shape (and size) change. We envision that dipole potential measurements could provide novel insights into micellar processes that are associated with dipolar reorganization.

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#### 1. Introduction

Micelles are formed due to self assembly of detergents (soluble amphiphiles) above a critical concentration (strictly speaking, a narrow concentration range), referred to as the critical micelle concentration (CMC) (Tanford, 1978). Micelles are popularly used as membrane-mimetics. This is due to a number of reasons which include their small size that results in optical transparency and lack of scattering, monodisperse nature, and ease of manipulation. A major use of micelles has been in studies of membrane proteins and peptides (Sham et al., 2003; Raghuraman and Chattopadhyay, 2004; Rawat et al., 2005). Another important use of micelles in membrane biology is in the overall context of solubilization and reconstitution of membrane proteins and receptors from native membranes (Kalipatnapu and Chattopadhyay, 2005; Chattopadhyay et al., 2015).

Structural transitions involving shape changes play an important role in cellular physiology (Paluch and Heisenberg, 2009). Such transitions can be conveniently induced in charged micelles

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http://dx.doi.org/10.1016/j.chemphyslip.2015.11.005 0009-3084/© 2015 Elsevier Ireland Ltd. All rights reserved. by increasing ionic strength of the medium (Mazer et al., 1976; Young et al., 1978; Hayashi and Ikeda, 1980; Rawat and Chattopadhyay, 1999; Heerklotz et al., 2004; Geng et al., 2005; Rawat et al., 2005; Arora-Sharawat and Chattopadhyay, 2007; Chaudhuri et al., 2009, 2012). For example, spherical charged micelles of sodium dodecyl sulfate (SDS, anionic) or cetyltrimethylammonium bromide (CTAB, cationic) that exist in water at concentrations higher than CMC assume an elongated rod-like (prolate) structure in the presence of high salt concentrations (see Fig. 1). This is due to reduced interactions among the charged headgroups because of the added salt. This is known as sphere-torod transition. Interestingly, this salt-induced micellar shape change is accompanied by a reduction in CMC (Chattopadhyay and London, 1984).

Dipole potential is the potential difference within the membrane bilayer and its origin lies in the nonrandom orientation of electric dipoles of membrane lipids, proteins and water molecules (Brockman, 1994; Clarke, 2001; O'Shea, 2005; Wang, 2012). Work from a number of laboratories has shown that membrane dipole potential is a sensitive indicator of the nature of membrane lipid (Cladera and O'Shea, 1998; Starke-Peterkovic et al., 2006; Starke-Peterkovic and Clarke, 2009; Haldar et al., 2012; Bandari et al., 2014), membrane protein function and lipid–protein interaction (Duffin et al., 2003; Starke-Peterkovic et al., 2005; Singh et al., 2013; Chaudhuri and Chattopadhyay, 2014; Clarke, 2015; Richens et al., 2015). We have recently introduced the



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Abbreviations: CMC, critical micelle concentration; CMT, critical micelle temperature; CTAB, cetyltrimethylammonium bromide; di-8-ANEPPS, 4-(2-(6-(dioctylamino)-2-naphthalenyl)ethenyl)-1-(3-sulfopropyl)-pyridinium inner salt; REES, red edge excitation shift; SDS, sodium dodecyl sulfate.



**Fig. 1.** (a) Chemical structures of representative detergents of two charge types used in this study. (b) A schematic representation of the sphere-to-rod transition in charged micelles induced by high ionic strength. The structural transition takes place in charged micelles (such as SDS or CTAB) at concentrations well above the critical micelle concentration. The microenvironment and packing of molecules in rod-shaped micelles are heterogeneous and are shown as spherical 'end caps' (darker shade) and the cylindrical central part (lighter shade). The headgroup spacing is reduced in the cylindrical part of the rod-shaped micelle due to attenuation of charge interactions by the added salt. Adapted and modified from Chaudhuri et al., 2012.

concept of membrane dipole potential in case of micelles (Sarkar and Chattopadhyay, 2015). In particular, we showed that the process of micellization, which is associated with dipolar rearrangement, could be followed by monitoring the change in micellar dipole potential, and this approach offers a novel way to measure CMC of detergents. In our continuing effort to understand micellar organization in terms of dipole potential, we show in this paper that micellar dipole potential is sensitive to sphere-to-rod transition of charged (SDS and CTAB) micelles, as measured by the dual wavelength ratiometric approach utilizing the potentialsensitive membrane probe di-8-ANEPPS.

#### 2. Materials and methods

#### 2.1. Materials

NaCl and KBr were obtained from Sigma Chemical Co. (St. Louis, MO). CTAB was purchased from Serva (Heidelberg, Germany). SDS was from Calbiochem (San Diego, CA). Di-8-ANEPPS was purchased from Molecular Probes/Invitrogen (Eugene, OR). All other chemicals used were of the highest available purity. Water was purified through a Millipore (Bedford, MA) Milli-Q system and used throughout.

#### 2.2. Methods

#### 2.2.1. Sample preparation

The concentrations of SDS (16 mM) and CTAB (6 mM) used were  $\sim$ 2 and 6 times their CMC, respectively, in order to ensure that they were in the micellar state and to achieve maximum extent of structural transition (see later). The molar ratios of di-8-ANEPPS to detergents (1:32,000 (mol/mol) for SDS micelles and 1:12,000 (mol/mol) for CTAB micelles) were carefully chosen to give optimum signal-to-noise ratio with minimal perturbation to the micellar organization and negligible interprobe interactions. In order to incorporate di-8-ANEPPS from a methanolic stock

solution was added to 2 ml of preformed micelles containing varying amounts of NaCl (for SDS micelles) or KBr (for CTAB micelles) and mixed well by vortexing for 1 min. The resultant di-8-ANEPPS concentration was  $0.5\,\mu M$  in all cases and methanol content was always low (0.5% v/v). The concentration of stock solution of di-8-ANEPPS in methanol was estimated from its molar extinction coefficient ( $\varepsilon$ ) of 37,000 M<sup>-1</sup> cm<sup>-1</sup> at 498 nm (Le Goff et al., 2007). Background samples were prepared the same way except that di-8-ANEPPS was not added to them. Samples were equilibrated in the dark for 12 h before measuring fluorescence. Experiments were performed with four sets of samples. Since the critical micelle temperature (CMT) of SDS in presence of 0.5 M NaCl (highest concentration of NaCl used) is 24.7 °C (Hayashi and Ikeda, 1980), all sample preparations and experiments were performed at  $\sim$ 25 °C. Similarly, experiments with CTAB micelles were performed at ~35 °C as precipitation readily occurs below this temperature (Debye and Anacker, 1951; Imae et al., 1985, 1988).

#### 2.2.2. Measurement of potential-sensitive fluorescence intensity ratio

Measurements were carried out by dual wavelength ratiometric approach using the voltage-sensitive fluorescence probe di-8-ANEPPS (Gross et al., 1994; Clarke and Kane 1997; Starke-Peterkovic et al., 2005, 2006; Haldar et al., 2012). Steady state fluorescence measurements were performed with a Hitachi F-7000 (Tokyo, Japan) spectrofluorometer using 1 cm path length quartz cuvettes at  $\sim$ 25 °C for experiments with SDS micelles and  $\sim$ 35 °C for experiments with CTAB micelles. This instrument is equipped with a magnetically stirred cuvette compartment thermostated with a circulating water bath. While heating, the sample temperature was continuously measured with a thermocouple. Excitation and emission slits with a bandpass of 5 nm were used for all measurements. Background intensities of samples were subtracted from each sample to cancel any contribution due to the solvent Raman peak. Fluorescence intensities were recorded at two excitation wavelengths (420 and 520 nm). Emission wavelength was fixed at 670 nm. The fluorescence ratio (R), defined as the ratio of fluorescence intensities at an excitation wavelength of 420 nm to that at 520 nm (emission at 670 nm in both cases) was calculated (Starke-Peterkovic et al., 2006), which is a measure of micellar dipole potential.

#### 3. Results and discussion

In order to monitor the change in dipole potential associated with the process of sphere-to-rod transition in charged micelles. we carried out micellar dipole potential measurements by a dual wavelength ratiometric approach using the voltage-sensitive (electrochromic) styrylpyridinium probe, di-8-ANEPPS (see inset in Fig. 2 for chemical structure) (Gross et al., 1994; Clarke and Kane, 1997; Starke-Peterkovic et al., 2005, 2006). For this, we selected representative detergents of different charge types (see Fig. 1a), *i.e.*, SDS (anionic) and CTAB (cationic) that are known to exhibit sphere-to-rod transition induced by salt (Hayashi and Ikeda, 1980; Imae et al., 1985). For experiments using SDS, we chose to carry out experiments with a detergent concentration that was  $\sim$ 2 times its CMC, since it corresponds to the critical concentration of SDS micelles that show maximum dissymmetry in its aspect ratio that is related to micellar shape (Hayashi and Ikeda, 1980). This also ensures that SDS was in the micellar state in all experiments. In case of CTAB micelles, maximum dissymmetry in aspect ratio in the presence of salt was earlier reported to be at a detergent concentration that was ~6 times its CMC (Imae et al., 1985). We therefore performed experiments with CTAB at a concentration that was  $\sim$ 6 times the CMC of CTAB.

The dual wavelength ratiometric technique utilizing di-8-ANEPPS is a popular approach to monitor dipole potential (Gross et al., 1994; Clarke and Kane 1997; Starke-Peterkovic et al., 2005, 2006; Haldar et al., 2012; Sarkar and Chattopadhyay, 2015). The main parameter in this method is the fluorescence ratio (*R*) which is the ratio of fluorescence intensities at an excitation wavelength of 420 nm to that at 520 nm, with emission wavelength being fixed at 670 nm. This ratio is sensitive to any change in the dipolar field where the potential-sensitive probe di-8-ANEPPS is localized, and is independent of specific molecular interactions (Gross et al., 1994; Robinson et al., 2011). The underlying mechanism for this phenomenon is believed to be electrochromic in nature, leading to a shift of the excitation spectrum of di-8-ANEPPS, the shift being



**Fig. 2.** Change in the fluorescence ratio (*R*) of the excitation spectra of di-8-ANEPPS (see inset for chemical structure) with increasing NaCl concentration for SDS micelles. The fluorescence ratio (*R*) is defined as the ratio of fluorescence intensities at an excitation wavelength of 420 nm to that at 520 nm (emission at 670 nm in both cases). Data points shown are means  $\pm$  S.E. of four independent measurements. The ratio of di-8-ANEPPS to SDS was 1:32,000 (mol/mol), and the concentration of SDS was 16 mM. Measurements were carried out at ~25 °C. The line joining the data points is provided merely as a viewing guide. See Section 2 for more details.

proportional to the local electric field strength (Loew et al., 1979; Le Goff et al., 2007). The fluorescence ratio is independent of small changes in dye concentration due to the use of two excitation wavelengths for measurement of fluorescence intensity (Clarke, 2010).

The variation in R of di-8-ANEPPS with increasing salt concentration for micelles of anionic SDS and cationic CTAB is shown in Figs. 2 and 3, respectively. The figures show that increasing ionic strength resulted in an increase in the fluorescence intensity ratio in both cases. This could be interpreted as an increase in micellar dipole potential in response to increasing salt concentration due to sphere-to-rod transition. The change in fluorescence intensity ratio was accompanied by  $\sim 2$  fold increase in fluorescence intensity of di-8-ANEPPS when the salt concentration was increased from 0 to 0.5 M, thereby implying a change in the immediate environment experienced by di-8-ANEPPS upon sphere-to-rod transition. This could imply a reduction in apparent polarity experienced by the probe in rod-shaped micelles, possibly due to a decrease in micellar water content in rod-shaped micelles. This is supported by our previous observation, using the polaritysensitive fluorescence probe pyrene, that the apparent dielectric constant is lowered by ~31% upon sphere-to-rod transition of SDS micelles (Chaudhuri et al., 2009). In the presence of salt, the electrostatic repulsion between charged headgroups of detergent monomers is attenuated due to shielding (screening) of charges, thereby reducing headgroup spacing in the cylindrical part of the rod shaped micelle (see Fig. 1b). It has been previously suggested that large rod-shaped micelles represent better models for biomembranes (Kalyanasundaram et al., 1975; Rawat and Chattopadhyay, 1999) due to the release of curvature stress encountered in spherical micelles, and the hydrocarbon chains are more ordered in rod-shaped micelles compared to spherical micelles (Heerklotz et al., 2004). Another reason for the reduction in polarity experienced by the probe upon sphere-to-rod transition could be deeper localization of the probe in rod-shaped micelles.

The increase in dipole potential upon micellar shape change merits comment. Figs. 2 and 3 show that the fluorescence intensity ratio was low for spherical micelles and exhibits increase with increase in salt concentration, irrespective of detergent charge. The fluorescence intensity ratio shows an overall increase of ~40%, independent of the detergent chosen, when the highest concentration (0.5 M) of salt (NaCl or KBr) was used (control experiment



**Fig. 3.** Change in the fluorescence ratio (*R*) of the excitation spectra of di-8-ANEPPS with increasing KBr concentration for CTAB micelles. The ratio of di-8-ANEPPS to CTAB was 1:12,000 (mol/mol), and the concentration of CTAB was 6 mM. Measurements were carried out at ~35 °C. All other conditions are as in Fig. 2. The line joining the data points is provided merely as a viewing guide. See Section 2 for more details.

with the neutral detergent Triton X-100 failed to show any appreciable increase in *R*). It has previously been shown that dipole potential of lipid vesicles is not affected at this concentration of salt (Clarke and Lüpfert, 1999). This suggests that micellar sphere-torod transition is accompanied by profound dipolar reorganization. Such structural transition in micelles results in larger sized micelles with greater aggregation number. For example, the aggregation number of SDS increases from 62 in spherical micelles (Helenius and Simons, 1975), to 480 in rod-shaped micelles (Mazer et al., 1976) in presence of 0.5 M NaCl. This implies that in the presence of salt, the electrostatic repulsion between charged headgroups of detergent monomers is reduced due to shielding of charges, which results in reduction in headgroup spacing, particularly in the cylindrical part of the rod shaped micelles (see Fig. 1b). A consequence of such an organizational change would be the dynamic restriction imposed on the mobility of the constituent monomers in the micellar assembly. This, in turn, would help to couple the motion of water molecules with the slow moving molecules in the micellar assembly (Bhattacharyya and Bagchi, 2000; Chattopadhyay and Haldar, 2014). We previously reported that such increase in confined water could be monitored by increased red edge excitation shift (REES) of fluorescent probes that sense the micellar interior (Rawat and Chattopadhyay, 1999; Arora-Sharawat and Chattopadhyay, 2007). REES represents the shift in the wavelength of maximum fluorescence emission toward higher wavelengths, caused by a shift in the excitation wavelength toward the red edge of the absorption band, and is an indicator of confined dipoles (water molecules) in an organized molecular assembly (Haldar et al., 2011).

The confined water creates a dipolar field that gives rise to higher dipole potential since dipole potential arises due to the *nonrandom* arrangement of micellar dipoles and water molecules at the micelle interface. In other words, spatial (due to micellar size) and temporal (due to slow time scales of restricted water molecules) restriction of water molecules with increasing ionic strength could result in a decrease in the population of randomly oriented water molecules, leading to an increase in dipole potential. To the best of our knowledge, such drastic changes in dipolar orientation giving rise to characteristic changes in dipole potential associated with micellar shape change has not been reported previously. In other words, a hallmark of sphere-to-rod transition is dipolar reorganization that results in higher values of micellar dipole potential.

Structural transitions involving shape changes assume relevance in cellular physiology during development (Paluch and Heisenberg, 2009). It has been previously reported that alteration of membrane cholesterol level, selective removal of phospholipids from the outer membrane leaflet, pH and membrane potential alterations, metabolic depletion and introduction of lysophospholipids, fatty acids, and charged amphipathic agents in membranes results in shape changes of erythrocytes (Kuypers et al., 1984; Gedde and Huestis, 1997; Backman et al., 1998). Importantly, shape changes in cellular membranes that occur due to modifications of membrane composition have been shown to directly affect the function of membrane proteins such as mechanosensitive channels that respond to changes in membrane curvature (Perozo et al., 2002).

Taken together, we report here that the process of micellar sphere-to-rod transition involves profound dipolar reorganization which gets manifested as change in micellar dipole potential, measured utilizing ratiometric fluorescence of the potentialsensitive probe di-8-ANEPPS. Our results therefore provide novel insight into dipolar rearrangements that take place during sphereto-rod transition in case of charged micelles. These results, along with our previous paper in which we showed that micellization is accompanied with dipolar rearrangement which allows measurement of CMC (Sarkar and Chattopadhyay, 2015), opens up a novel window for monitoring micellar dynamics and organization using dipolar reorganization. This will complement the ongoing work on membrane dipole potential (Haldar et al., 2012; Richens et al., 2015; Clarke, 2015). Future applications of such an approach to explore physiologically relevant shape changes in the cellular milieu represents an exciting challenge.

#### **Conflict of interest**

The authors declare no conflict of interest.

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