Electronic Supplementary Information

How do the interfacial properties of zwitterionic sulfobetaine micelles differ from those of cationic alkyl quaternary ammonium micelles? an excited state proton transfer study

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Figure S7. Fluorescence anisotropy decay of MPTS inside micelles with variation of the tail length of the surfactant ($\lambda em = 440$ nm).



Figure S8. Histogram of size distribution of different micelles obtained from dynamic light scattering measurements.

Table S1: Hydrodynamic diameter of micelle along with the observed polydispersity index.

	Size, d nm	PDI
CTAB,	4.9 ± 1 nm	0.473
20mM		
<i>SB16</i> ,	5.6 ± 1 nm	0.266
20mM		
DTAB,	$3.6 \pm 1 \text{ nm}$	0.234
30mM		
<i>SB12,</i>	4.8 ± 1 nm	0.316
20mM		

Determination of pKa of HPTS:

HPTS is a pH sensitive probe. In bulk water at low pH HPTS absorbs at 403nm; but with the increment of pH to basic side a new absorption maximum arise at 450 nm with concomitant disappearance of absorption band at 403nm. If we represent HPTS in acid form as HA and its basic form as A^- , then the following equilibrium describes the chemical reaction that occurs as the [H⁺] is changed.

HA (aq)
$$\longrightarrow$$
 H⁺ (aq) + A⁻ (aq)

The acid dissociation equilibrium constant (K_a) for the fluorophore can be expressed as

$$K_{a} = \frac{[H^{+}][A^{-}]}{[HA]}$$
(1)
$$- \log K_{a} = -\log [H^{+}] - \log \left(\frac{[A^{-}]}{[HA]} \right)$$
(2)
$$pK_{a} = p^{H} - \log \left(\frac{[A^{-}]_{455}}{[HA]_{405}} \right)$$
(3)

We consider absorbance for each pH at 405nm for HA and 455 nm for A^- .



Figure S9: (a) Absorption spectra of HPTS in water at different pH; (b) the plot of $\log([A^-]/[HA])$ vs. pH of HPTS in water, CTAB and SB16 micelles showing different pK_a values.

Analysis of the anisotropy data by Wobbling-in-cone model

The observed anisotropy decay, r(t) is a product of three motions,⁴⁰⁻⁴²

$$r(t) = r_W(t) r_D(t) r_M(t)$$
 (3)

r(t) may also be written in terms of the order parameter S

$$\mathbf{r}(t) = \mathbf{r}_0 \left[\mathbf{S}^2 + (1 - \mathbf{S}^2) \exp(-t/\tau_W) \right] \exp(-t(1/\tau_D + 1/\tau_M))$$
(4)

S is related to the semicone angle θ as

$$S = 0.5 \cos\theta (1 + \cos\theta) \tag{5}$$

The time constant (τ_M) of the overall rotation of the micelle is given by

$$\tau_M = \frac{4\eta\pi r_h^3}{3k_B T} \tag{6}$$

where, η = viscosity of solution and r_h is the hydrodynamic radius of the micelle. We used dynamics light scattering (DLS) measurements to obtain the hydrodynamic diameter of the micelles. The results are added in the supporting information (Figure S6 and Table S1).

Comparing equations (2) and (4), we obtain,

$$\beta = S^2 \tag{7}$$

$$1/\tau_{\rm f} = 1/\tau_{\rm W} + 1/\tau_{\rm D} + 1/\tau_{\rm M} \tag{8}$$

$$1/\tau_{\rm s} = 1/\tau_{\rm D} + 1/\tau_{\rm M}$$
 (9)

All the analyzed parameters are given in table 3. The semicone angles are very similar for all the micelles indicating a close similarity of the local environments. However, the wobbling and the translational time constants differ significantly among different micelles. In the zwitterionic micelles, the wobbling time constants and the translational time constants are longer than the corresponding cationic micelles (Table 3).

The diffusion coefficient for wobbling (D_W) of HPTS inside different micelles can be obtained by the relation

$$D_{w} = \left\{ \tau_{R} \left(1 - \beta \right) \right\}^{-1} \left[\frac{x^{2} \left(1 + x \right)^{2}}{2 \left(x - 1 \right)} \left\{ \ln \left(\frac{1 + x}{2} \right) + \left(\frac{1 - x}{2} \right) \right\} + \left(\frac{1 - x}{24} \right) \left(6 + 8x - x^{2} - 12x^{3} - 7x^{4} \right) \right]$$
(10)

where, $x = \cos\theta$.