

# Spontaneous Formation of Multi-Architecture Vesicles of $[C_8mim]Br$ + $[Na]DBS$ in Aqueous Medium: Synergic Interplay of Electrostatic, Hydrophobic and $\pi$ - $\pi$ Stacking Interactions

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## Supporting information

## Annexure 1

1. The Adsorption efficiency of surfactant at air-water interface is estimated by measuring  $pC_{20}$  using the relation (1)<sup>1,2</sup>

where,  $C_{20}$  is the concentration needed to reduce the surface tension of the solvent (water in the present case) by  $20\text{mN.m}^{-1}$ . The higher  $pC_{20}$  value indicates high adsorption efficiency of the surfactant.<sup>3</sup>

2. Effectiveness of surface tension reduction is the other parameter that measures the adsorption efficiency of a surfactant, denoted by  $\pi_{CMC}$  and calculated using the relation (2).<sup>1,4</sup>

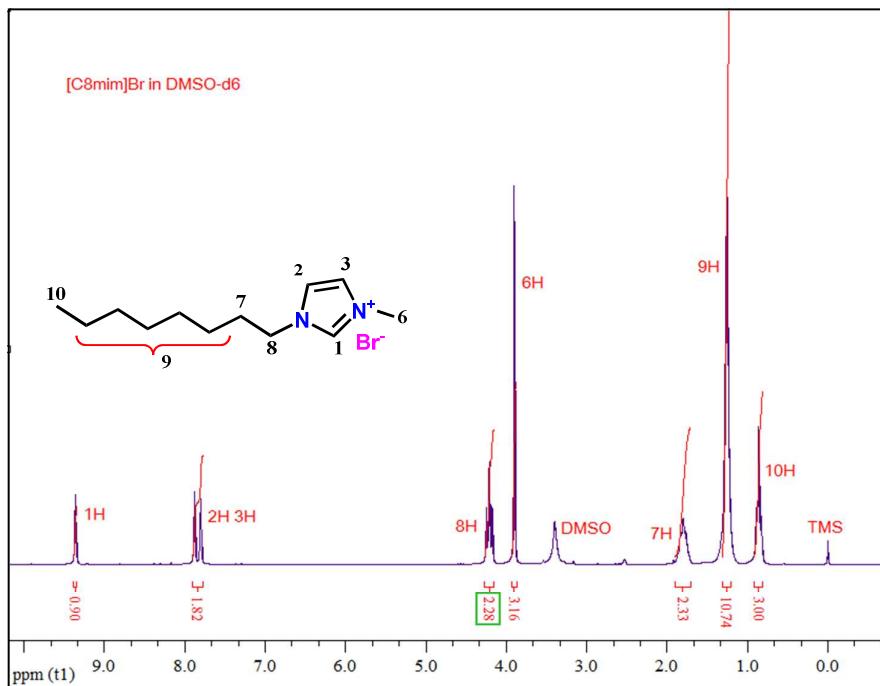
where  $\gamma_{H_2O}$  stands for the surface tension of the pure water and  $\gamma_{CAC}$  stands for the surface tension of the solvent medium at CAC.

3. The amount of surfactants adsorbed at the interface is estimated from relative surface excess concentration ( $\Gamma_{\max}^{tot}$ ). The values  $\Gamma_{\max}^{tot}$  of at the CMC have been calculated using Gibbs adsorption Eq. 3 from the least-squares slope of the  $\gamma$  versus  $\log C$  plot.

Where “ $\partial\gamma/\partial \ln C$ ” is the slope of  $\gamma - \ln C$  plot in the pre *CMC* region.<sup>5-7</sup> and n is Gibbs adsorption coefficient. In the current paper it is used from the mole fraction value of surfactants<sup>8</sup> using the relation,  $n = \sum_i r^i x^i$ , where  $r^i$  and  $x^i$  correspond to the number of species formed from the  $i^{\text{th}}$  component and the mole fraction of the  $i^{\text{th}}$  component respectively.

4. Minimum area occupied by monomers at the interface was calculated using equation 4.

Where  $N_A$  is Avogadro number and the factor of  $10^{16}$  arises as a conversion factor of area from  $\text{nm}^2$  to  $\text{\AA}^2$ .

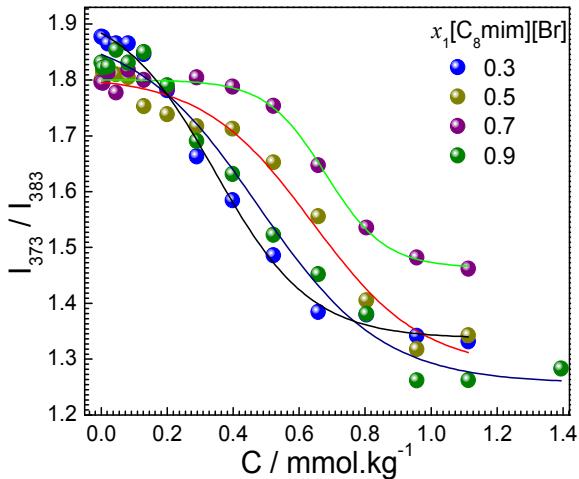


**Figure S1.** NMR spectra of synthesised [C<sub>8</sub>mim]Br

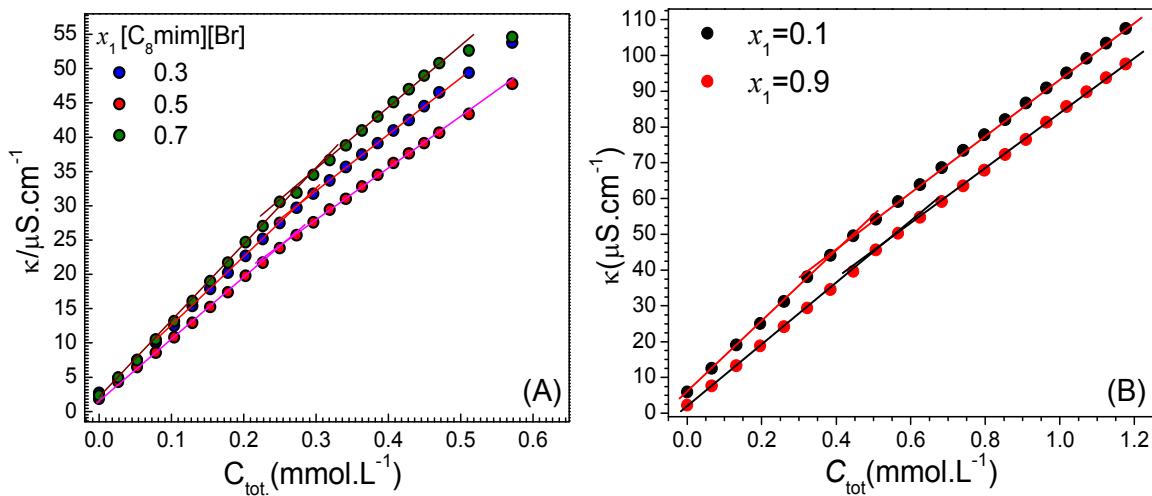
## 2.1. $^1\text{H}$ NMR chemical shifts Data.

[C<sub>8</sub>mim]Br,  $^1\text{H}$ -NMR: 200MHz (DMSO-d<sub>6</sub>):  $\delta_{\text{H}}$  (ppm) 9.361 (s, 1H), 7.879(d, 2H), 4.212(t, 2H), 3.901(s, 3H), 1.798(t, 2H), 1.255(m, 10H), 0.859(t, 3H).

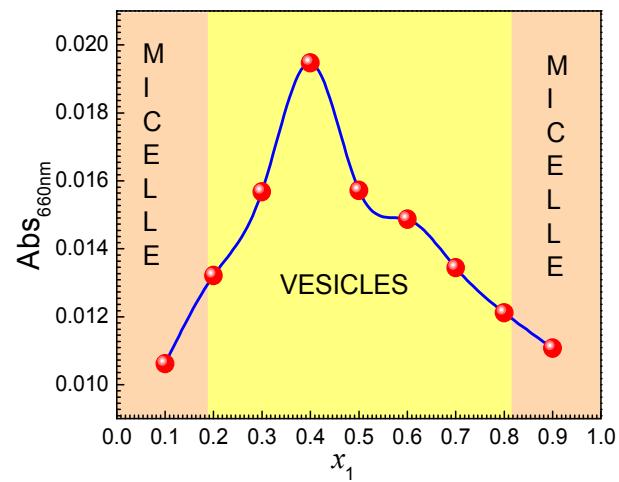
**ESI-MS:** [C<sub>8</sub>mim]<sup>+</sup> m/z:195.19



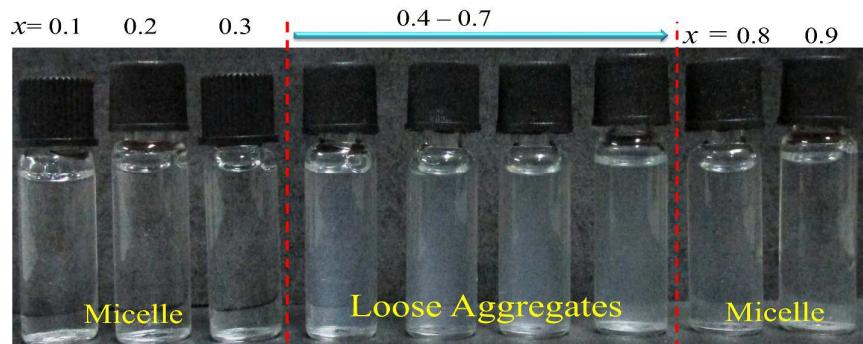
**Figure S2.** Plot showing variation in ratio of  $I_1/I_3$  vibronic bands of pyrene as a function of mixtures concentrations at different mole fractions. CAC were obtained from the first derivative of  $I_1/I_3$  vs concentration curve.



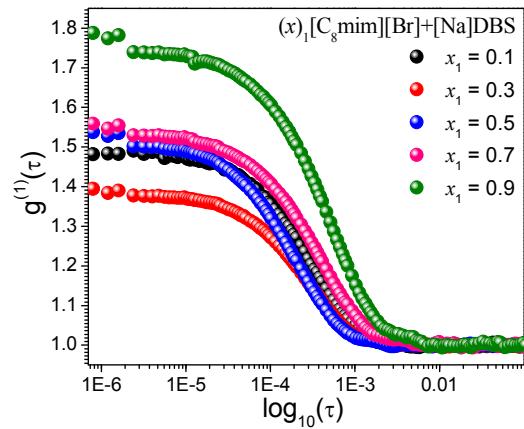
**Figure S3.** Conductometric determination of the CAC of [C<sub>8</sub>mim]Br+[Na]DBS mixtures at different mole fractions at 298 K.



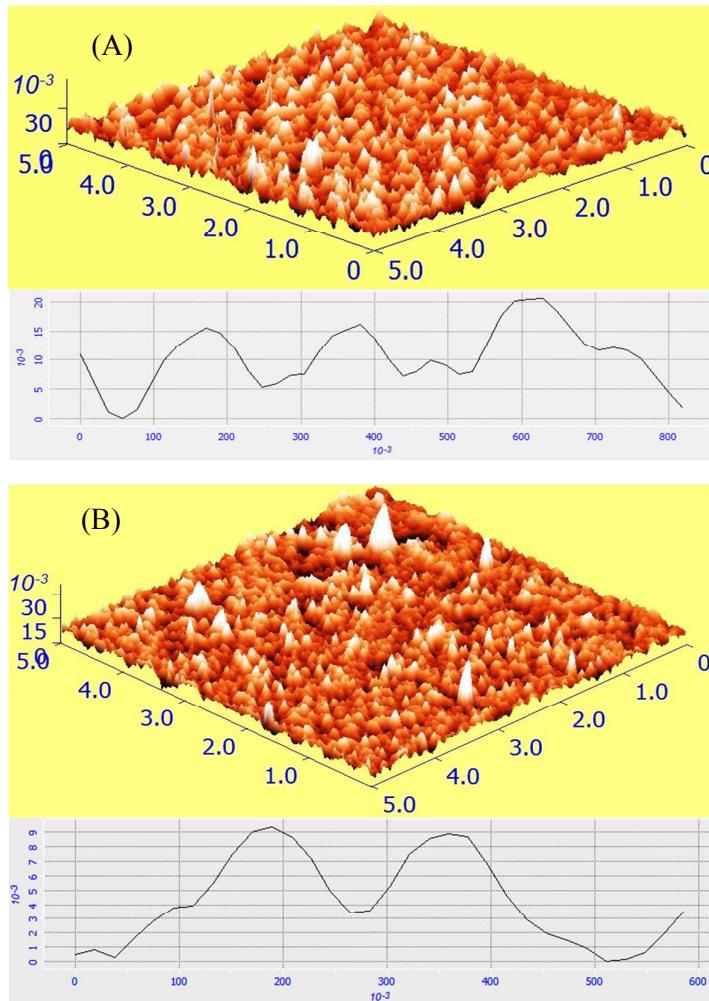
**Figure S4.** Turbidity measurement of cat-anionic mixture of  $[\text{C}_8\text{mim}]\text{Br} + [\text{Na}]\text{DBS}$ .



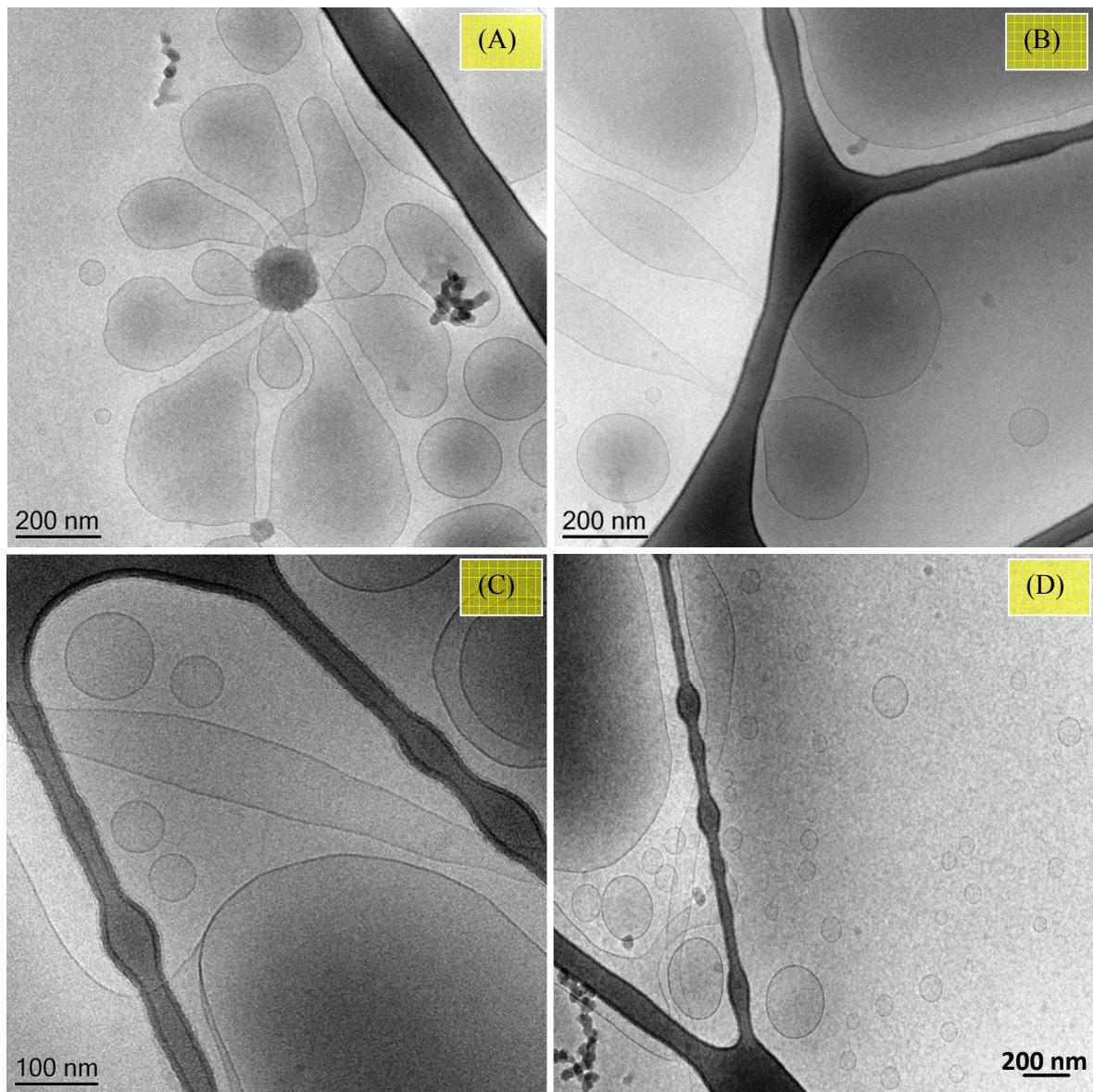
**Figure S5.** Digital images of  $[\text{C}_8\text{mim}]\text{Br} + \text{Na}[\text{DS}]$  mixtures at different mole fraction of  $[\text{C}_8\text{mim}]\text{Br}$ .



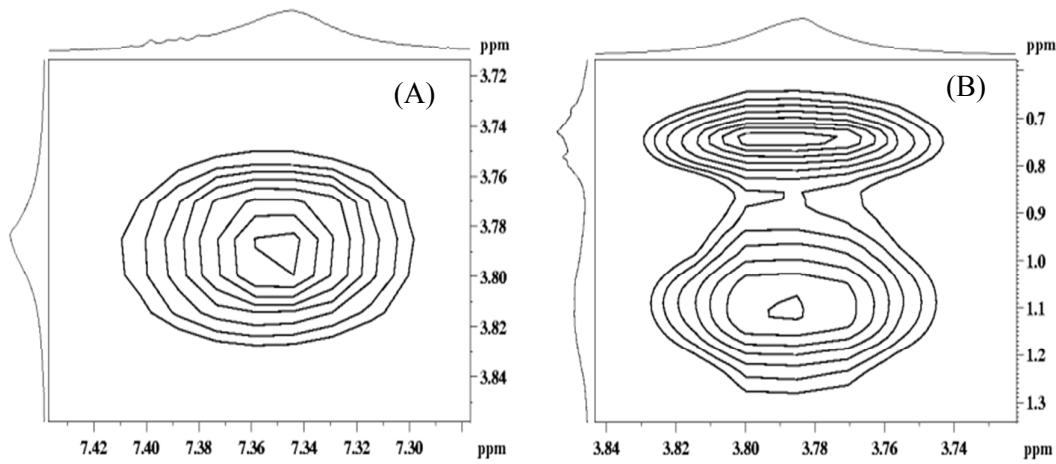
**Figure S6.** Intensity autocorrelation functions of  $[\text{C}_8\text{mim}][\text{Br}] + \text{Na}[\text{DBS}]$  mixed micelles and vesicles at various mole fraction of  $[\text{C}_8\text{mim}][\text{Br}]$ .



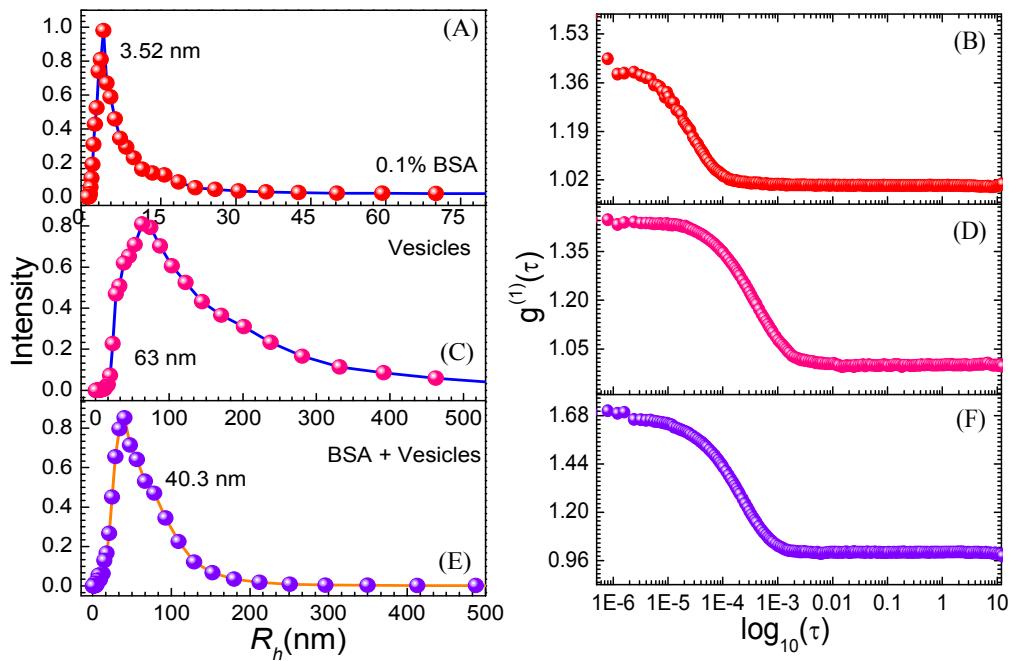
**Figure S7.** 3-D AFM images showing of mixed micelles along with height profiles of  $[\text{C}_8\text{mim}][\text{Br}]+[\text{Na}]$ DBS mixture at (A)  $x_1=0.1$  and (B)  $x_1=0.9$  mole fraction of  $[\text{C}_8\text{mim}][\text{Br}]$ .



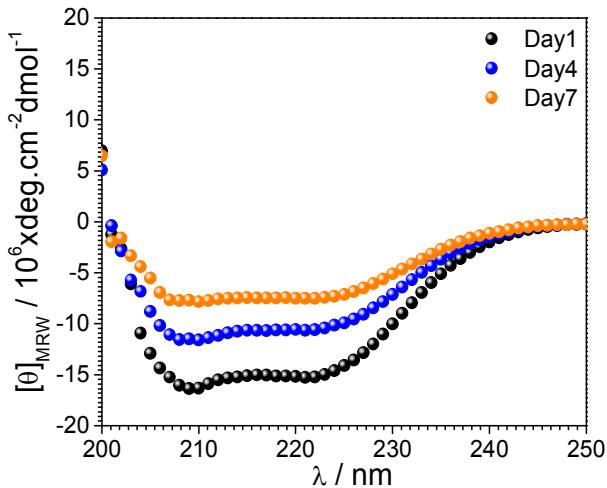
**Figure S8.** Cryo-TEM images showing unilamellar vesicles of different architectures, sphere and tubules and ribbons.



**Figure S9.** NOESY spectra in expanded form for the  $[C_8\text{mim}]Br + [Na]\text{DBS}$  ( $10\text{mmol.L}^{-1}$ ) mixture at  $x=0.5$  of  $[C_8\text{mim}]Br$  in  $D_2O$ . NOESY spectra show interaction of N-CH<sub>3</sub> with (A) aromatic region and (B) alkyl chain.



**Figure S10.** Hydrodynamic radii and corresponding intensity correlation function of (A), (B) 0.1% BSA (C), (D)  $[C_8\text{mim}]Br + [Na]\text{DBS}$  vesicles ( $2\text{ mmol.L}^{-1}$ ) and (E), (F) BSA + vesicles



**Figure S11.** CD spectra of 0.1% BSA in buffer solution as a function of time (days).

## REFERENCES:

1. Luezak, J.; Hupka, J.; Thoming, J.; Jungnickel, C. Self organization of imidazolium ionic liquids in aqueous solution. *Colloid and Surface A: Physicochemical and Engineering Aspects*, **2008**, 3, 125-133.
2. Rosen, M. J. *Surfactants and Interfacial Phenomena*, second ed., Wiley, New York, **1989**.
3. Comelles, F.; Ribosa, I.; González, J. J.; Garcia, M. Micellization of sodium lauryl ether sulphate (SLES) and short chain imidazolium ionic liquids in aqueous solution, *J. Colloid Interface Sci.* **2014**, 425, 44-51.

4. Jiao, J.; Dong, B.; Zhang, H.; Zhao, Y.; Wang, X.; Wang, R.; Yu, L. Aggregation Behaviours of Dodecyl Sulfate-Based Anionic Surface Active Ionic Liquids in Water. *J. Phys. Chem. B* **2012**, *116*, 958-965.
5. Mondal, J. H.; Ahmed, S.; Das, D. Physicochemical Analysis of Mixed Micelles of a Viologen Surfactant: Extended to Water-in-Oil (w/o) Microemulsion and Cucurbit [8] uril-Assisted Vesicle Formation. *Langmuir* **2014**, *30*, 8290-8299.
6. Pan, A.; Sil, P.; Dutta, S.; Das, P. K.; Bhattacharya, S. C.; Rakshit, A. K.; Aswal, V. K.; Moulik, S. P. Micellization of Cetyltrimethylammonium Bromide: Effect of Small Chain Bola Electrolytes. *J. Phys. Chem. B* **2014**, *118*, 3041-3052.
7. Eastoe, J.; Nave, S.; Downer, A.; Paul, A.; Rankin, A.; Tribe, K.; Penfold, J.; Adsorption of Ionic Surfactants at the Air–Solution Interface. *Langmuir* **2000**, *16*, 4511-4518.
8. Mukherjee, I.; Moulik, S. P.; Rakshit, A. K. Tensiometric Determination of Gibbs Surface Excess and Micelle Point: A Critical Revisit. *J. Colloid Interface Sci.* **2013**, *394*, 329-336