

Micellization of Cetyltrimethylammonium Bromide: Effect of Small Chain Bola Electrolytes

Animesh Pan,[†] Pallabi Sil,[†] Sounak Dutta,[‡] Prasanta Kumar Das,[‡] Subhash Chandra Bhattacharya,[†] Animesh Kumar Rakshit,[§] Vinod Kumar Aswal,^{||} and Satya Priya Moulik^{*,†}

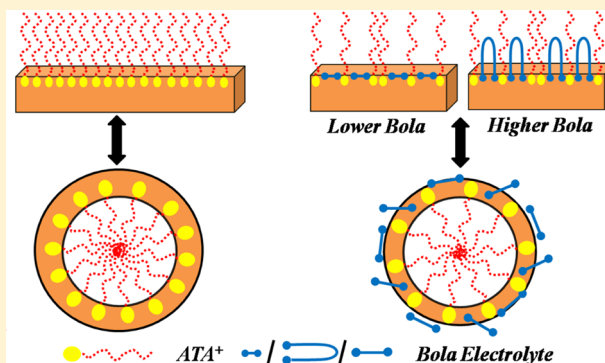
[†]Centre for Surface Science and [§]Indian Society for Surface Science & Technology, Department of Chemistry, Jadavpur University, Kolkata 700 032, India

[‡]Department of Biological Chemistry, Indian Association for Cultivation of Science, Kolkata 700 032, India

^{||}Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

S Supporting Information

ABSTRACT: Sodium dicarboxylates (or Bola salts) with methylene spacers 0, 2, 4, 6, 8, and 10 were studied in aqueous solution to investigate their influence on the micellization of cetyltrimethylammonium bromide (CTAB). Since bolas with spacer length ≤ 12 are known not to micellize in general, the herein used sodium dicarboxylates were treated as 2:1 amphiphilic electrolytes which reduced surface tension of water (except sodium oxalate with zero spacer) without self-association. Their concentration dependent conductance was also linear without breaks. The bolas affected the micellization of CTAB but acted like salts to decrease its CMC. Their combinations did not form bilayer aggregates as found in vesicles. Nevertheless, they synergistically interacted with CTAB at the air/water interface as revealed from Rosen's thermodynamic model. Hydrodynamic radius (R_h), Zeta-potential (ζ), and electrical double layer behavior of bola interacted CTAB micelles were assessed. From SANS measurements, micelle shape, shape parameters, aggregation number (N_{agg}), surface charge of the bola influenced CTAB micelles were also determined. NMR study as well supported the non-mixing of bolas with the CTAB micelles. They interacted in solution like "amphiphilic electrolytes" to influence the surface and micelle forming properties of CTAB.



1. INTRODUCTION

Cetyltrimethylammonium bromide (CTAB) with a 16 methylene chain and a quaternary ammonium cationic headgroup micellizes at ~ 1 mM at 25 °C in aqueous medium. Like other ionic surfactants, its micellization gets reduced in the presence of added salt by the electrostatic screening of the headgroup charge.^{1,2} It may form mixed micelles with nonionic and other cationic surfactants.^{3,4} With anionic surfactants it may form amphiphilic ion pairs, which at 1:1 molar ratio can form coacervates imparting turbidity in solution;^{5,6} even precipitation may result as a consequence.⁷ At uneven ratios (one is fairly greater than the other), formation of mixed compartmentalized entities between the two is also possible.^{8,9}

Amphiphiles having two functional headgroups at both ends of their chain are called bola amphiphiles; if the headgroups are ionic, then they are called bola electrolytes.^{10,11} It is known that bola electrolytes or "bolas" having methylene spacers ≥ 12 can form micelles.^{12–14} Lower bolas do not self-associate in general, but in the presence of salt, they may form micelles.^{15,16} Thus, $\text{Br}^-\text{Me}_3\text{N}^+(\text{CH}_2)_{10}\text{N}^+\text{Me}_3\text{Br}^-$ and $\text{Br}^-\text{Me}_3\text{N}^+(\text{CH}_2)_{10}\text{COO}^-\text{Na}^+$ do not form micelles in the temperature range of 298–308 K, whereas $\text{Br}^-\text{Me}_3\text{N}^+(\text{CH}_2)_{10}\text{OH}$ forms micelles

at ≥ 308 K. These bolaforms also self-associate in the presence of 10 mM NaBr at 303 K.¹⁷ Bolas with methylene spacers higher than 10 are reported to form mixed micelles with conventional surfactants, as well as form elongated aggregates, vesicles, tubes, and fibers.^{18–21} Long chain mono- and dicarboxylic acids can form stable vesicles in combination with alkyltrimethylammonium amphiphiles,²² but such studies with small chain bola fatty acids and their salts are not found in the literature. Bhattacharya et al.²³ reported bilayer or vesicle formation of bolaphile–amphiphile ion pairs between $\text{C}_6\text{H}_4(\text{O}(\text{CH}_2)_{10}\text{COO}^-)_2$ and $n\text{-C}_{16}\text{H}_{33}\text{NMe}_3^+$. They also studied the morphology and bilayer properties of vesicles formed from ion-paired amphiphiles of cationic gemini surfactants with palmitic acids in aqueous medium.²⁴ Similar and comparable other systems were also investigated by them^{25,26} and others.^{27,28} This has motivated us to study the bulk and interfacial behavior of small chain bola salts (sodium dicarboxylates) and their effect on the self-aggregation of CTAB in aqueous solution.

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We may herein add that CTAB can undergo a postmicellar transition at almost 0.15 mol/kg.²⁹ In this study we have studied mixed CTAB and bola at a total concentration of 0.05 mol/kg (in SANS experiments); in the other experiments, the concentrations were kept much smaller. Our objective was to study the properties of CTAB in bola environment close to its CMC, and not at higher concentration to avoid the post micellar transition. Conductometric, tensiometric, DLS, SANS, and NMR techniques were used in this endeavour. Since the bola salts used were nonaggregating in the studied range of concentration, they were expected to behave as “amphiphilic electrolytes” to affect the micellization of CTAB. The interaction produced neither coacervates nor bilayer aggregates, i.e., vesicles.

2. EXPERIMENTAL SECTION

2.1. Materials. Cetyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium bromide (DTAB) were obtained from Sigma Aldrich (USA). They were 99% pure and were used as received. Sodium oxalate and sodium succinate with 99% purity were obtained from Merck, India, and were used as received. Other dicarboxylic acids, e.g., adipic acid, suberic acid, sebacic acid, and dodecane dioic acid, were purchased from Sigma Aldrich (USA), and these acids were neutralized by NaOH addition and then lyophilized to obtain the desired product of sodium salt of different dicarboxylates. 1,6-Diphenyl-1,3,5-hexatriene (DPH) and Rhodamine6G (R6G) are obtained from Sigma Aldrich (USA). Double-distilled conductivity water (specific conductance, $\kappa = 2\text{--}3\ \mu\text{S cm}^{-1}$ at 303 K) was used in the experiments and D₂O was also purchased from Sigma-Aldrich (USA).

2.1.1. Characterization of the Amphiphilic Dicarboxylates. *Adipic Acid Disodium Salt (bola-4).* ¹H NMR (500 MHz, D₂O, rt) $\delta = 1.45\text{--}1.47$ (m, 4H), 2.10 (s, 4H); MS (ESI): m/z calcd for C₆H₈Na₂O₄: 190.0218 [M^+]; found: 190.9377 [$M^+ + 1$]. Anal Calc (%) for C₆H₈Na₂O₄: C, 37.91; H, 4.24; Found: C, 37.93; H, 4.28.

Suberic Acid Disodium Salt (bola-6). ¹H NMR (500 MHz, D₂O, rt) $\delta = 1.23$ (s, 4H), 1.47 (s, 4H), 2.07–2.12 (t, 4H); MS (ESI): m/z calcd for C₈H₁₂Na₂O₄: 218.0531 [M^+]; found: 219.1232 [$M^+ + 1$]. Anal Calc (%) for C₈H₁₂Na₂O₄: C, 44.04; H, 5.54; Found: C, 44.09; H, 5.51.

Sebacic Acid Disodium Salt (bola-8). ¹H NMR (500 MHz, D₂O, rt) $\delta = 1.22$ (s, 8H), 1.43–1.48 (m, 4H), 2.06–2.11 (t, 4H); MS (ESI): m/z calcd for C₁₀H₁₆Na₂O₄: 246.0844 [M^+]; found: 247.1073 [$M^+ + 1$]. Anal Calc (%) for C₁₀H₁₆Na₂O₄: C, 48.78; H, 6.55; Found: C, 48.73; H, 6.58.

Dodecanedioic Acid Disodium Salt (bola-10). ¹H NMR (500 MHz, D₂O, rt) $\delta = 1.23$ (s, 12H), 1.45–1.50 (m, 4H), 2.08–2.13 (t, 4H); MS (ESI): m/z calcd for C₁₂H₂₀Na₂O₄: 274.1157 [M^+]; found: 275.1141 [$M^+ + 1$]. Anal Calc (%) for C₁₂H₂₀Na₂O₄: C, 52.55; H, 7.35; Found: C, 52.52; H, 7.39.

The above characteristic results have confirmed the high purity of the herein synthesized bola electrolytes.

2.2. Methods. **2.2.1. Conductometry.** Conductometry experiments were done with a (EUTECH, Singapore) conductometer using a dip-type cell of cell constant = 1 cm⁻¹. All measurements were taken in a double-walled glass container at 303 K maintained by a Hahntech, DC-2006 circulating bath with an accuracy of ± 0.1 K. Concentrated surfactant solution was progressively added to 6 mL of water using a Hamilton microsyringe. Results were graphically processed by plotting specific conductance (κ) vs C_{total} to evaluate CMC from the inflection point.³⁰ The micellar ionization degree and hence the

extent of counterion binding of micelle (β) was determined by the slope ratio method (ratio between the slopes of the post and the pre CMC linear courses) described and discussed in the literature³¹ and cited by others.^{4,32} Reproducibility of results were checked from two to three repeat experiments.

2.2.2. Tensiometry. Tensiometric measurements were taken in a calibrated du Noüy tensiometer (Krüss, Germany). Conductivity of water (6 mL) was taken in a double-wall jacketed container placed in a thermostatted water-bath at 303 ± 0.1 K into which a stock solution of (bola or bola mixed with CTAB) of desired concentration was added in aliquots with a Hamilton microsyringe as required (allowing ~ 10 min for mixing and thermal equilibration). The surface tension was then measured, the details of which can be found elsewhere.³³ Surface tension (γ) values determined were accurate within ± 0.1 mN m⁻¹. Experiments were duplicated to check reproducibility.

2.2.3. Dynamic Light Scattering (DLS). A Nano ZS Zetasizer (Malvern, UK) was employed for dynamic light scattering measurements at 90° scattering angle with a He–Ne laser ($\lambda = 632.8$ nm). All experimental solutions were filtered 2–3 times through membrane filters (with pore size 0.25 μm) to remove dust particles. The mean values of triplicate experimental results are reported. For determination of zeta potential, 1.5 mL of 10 mM micellar solution was placed in the electrophoretic cell.

2.2.4. Small Angle Neutron Scattering (SANS). Small angle neutron scattering experiments were performed with a SANS diffractometer at the Dhruva reactor, Bhabha Atomic Research Centre, Trombay, Mumbai (India). The diffractometer makes use of a beryllium oxide filtered beam with a mean wavelength ($\lambda = 5.2$ Å). The angular distribution of scattered neutrons was recorded using a one-dimensional position sensitive detector (PSD). The accessible wave vector transfer ($q = 4\pi \sin \theta / \lambda$, where 2θ is the scattering angle) and the range of the diffractometer is 0.017–0.35 Å⁻¹. The PSD allows simultaneous recording of data over the full q range. The samples were held in a quartz sample holder of 0.5 cm thickness. The experimental temperature was kept fixed at 303 K. Measured SANS data were corrected and normalized to absolute units (as cross-section per unit volume) using standard procedure.³⁴

2.2.5. Nuclear Magnetic Resonance (NMR). NMR spectra were recorded in an Avance (Bruker) spectrometer operating at 500 MHz. Chemical shifts were determined using D₂O as internal locking agent for ¹H and 2D-NOESY NMR. Tetramethylsilane (TMS) was used as an internal chemical shift reference.

2.2.6. Mass Spectra and Elemental Analysis. High resolution mass spectrometric (HRMS) data were acquired by electrospray ionization (ESI) techniques, both in the positive and in the negative mode in a Q-tof Micro-Quadrupole mass spectrophotometer (Micromass, U.K.), and the element analyses were done in a Perkin-Elmer CHN Analyzer.

2.2.7. Absorbance and Fluorescence Measurements. Absorption spectra were taken using a SHIMADZU, UV-1601 (Japan) spectrophotometer at desired temperature using quartz cuvettes of 1 cm path length and steady-state fluorescence measurements were performed using a Perkin-Elmer LS 55 (USA) fluorescence spectrophotometer with an attachment of Fluorescence Peltier System PTP-1 using glass cell of 1 cm path length.

Steady-state fluorescence anisotropy (r_{ss}) measurements were taken with a polarization filter having the “L-format” configuration to measure the r_{ss} (fluorescence anisotropy) of the probe DPH. The anisotropy relation is expressed as³⁵

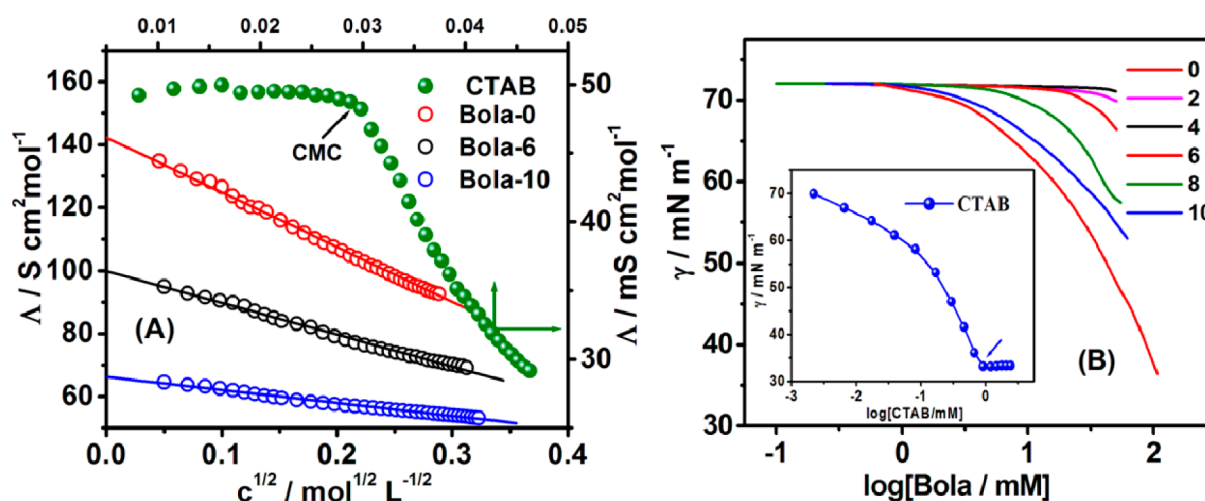


Figure 1. (A) Equivalent conductance (Λ) vs concentration plots of pure bolas like bola-0, bola-6, and bola-10 as well as that of CTAB. (B) Tensiometric profiles of pure bolas with different spacers. (Inset: tensiometric profile of CTAB.)

$$r_{ss} = \frac{I_{VV} - GI_{VH}}{I_{VV} - 2GI_{VH}} \quad (1)$$

where I_{VV} and I_{VH} are the vertically and horizontally polarized emission intensities, respectively, resulting from vertically polarized excitation of the probe. The expressions for the G factor I_{HV} and I_{HH} are similarly the vertically and horizontally polarized emissions resulting from horizontally polarized excitation, respectively. The anisotropy values were averaged over an integration time of 20 s and a maximum number of three measurements were taken for each sample. The anisotropy values of the probe in micellar media as presented in this work are the mean value of three individual determinations.

3. RESULTS AND DISCUSSION

3.1. Solution Properties of the Bolas. The bola electrolytes (dicarboxylates) with spacers 0–10 are soluble in water, but those with spacer number >10 are sparingly soluble and herein not considered. Conductance and surface tension methods were used to examine their bulk and interfacial properties. Conductance of bolas continued to smoothly change without break as illustrated in Figure 1A. Both specific and equivalent conductance plots supported the conclusion. Equivalent conductance plot of CTAB produced a break indicating micelle formation.

Surface tension (γ) of solutions (except oxalate) decreased with increasing [bola] but also did not produce breaks to witness formation of critical micelle concentration or CMC. Higher bolas than oxalate at equal concentration decreased γ more, indicating their higher surface activity (Figure 1B) because of increasing number of methylene groups, i.e., increasing hydrophobicity. In the inset of Figure 1B the tensiometric profile of CTAB is also presented to make a contrasting comparison with the bolas.

The concentration ratios between two successive bolas, i.e., bola-2/bola-4, bola-4/bola-6, bola-6/bola-8, and bola-8/bola-10 at a constant surface tension, e.g., $\gamma = 70 \text{ mN m}^{-1}$, were 1.7, 2.9, 3.0, and 1.2, respectively. According to Traube's rule³⁶ the ratios should have been 9.0. Hence, the surface activities of the bolas were different from single headed normal amphiphiles. According to Brown et al.³⁷ diammonium salts with ten carbon atoms between the ionic groups behave like normal electrolytes and did not form micelles. Yiv et al.¹² also observed similar

behavior of a diammonium bola salt with 12 methylene groups as the spacer. We have observed that $(\text{CH}_2)_{10}(\text{Me}_3\text{N}^+\text{Br}^-)_2$ and $\text{Br}^-\text{Me}_3\text{N}^+(\text{CH}_2)_{10}\text{COO}^-\text{Na}^+$ did not form micelles in aqueous medium in the temperature range of 293–308 K, but in the presence of 10 mM NaBr they showed self-aggregation.¹⁷ Addition of salt NaBr up to 10 mM did not help to form micelles of the herein studied bolas with spacer 10, and the question of self-assembly of lower bolas did not arise.

Direct support to the above solution behavior of bolas was obtained from DLS measurements. The studied solutions of bolas in water up to 0.2 M produced no scattering. Their assembly formation in aqueous medium was not supported. They behaved as strong electrolytes (amphiphilic electrolytes) in solution and influenced the micellization properties of CTAB discussed in detail in the following section.

3.2. CTAB–Bola Electrolyte Mixed Systems. We have made a detailed conductometric and tensiometric study of the mixed anionic bolas and cationic CTAB at various mole ratios between 0.1 and 0.9. Findings on the mixed oxalate (bola-0) and CTAB are presented in Figure 2A. The response of conductance on the CMC formation was not found at mole ratios up to 1:7, i.e., 0.125 (X_{CTAB}):0.875 (X_{bola}). Similar were the observations with bola-2, 4, and 6; responses of bola-8 and 10 started after 1:9 ratios, i.e., 0.1 (X_{CTAB}):0.9 (X_{bola}). Conductance results on bola-6 and 10 are shown in Figure 2B and C, respectively. Surface tension responded to all the studied ratios to produce CMC. It was observed that γ gradually decreased with formation of convex type curves until it reached a break point (CMC point), and the curves became flat thereafter. Results with bola 0, 6, and 10 are presented in Figure 2D, E, and F, respectively. The CMC values of bola-6 are presented in Table 1; the rest (for bolas 0, 2, 4, 8, and 10) are shown in SI Tables 1–5.

Results presented in Figure 2 and Table 1 (also SI Tables 1–5) revealed that, with increased mole fraction of CTAB in the mixed systems, the CMC increased. CMC values by the two methods were close; their mean values were used in data processing and analysis. At mole fraction 0.5 the decrease in surface tension by the bolas up to CMC was $\sim 40 \text{ dyn cm}^{-1}$; comparable values of γ were also observed at other mole fractions. The CTAB-bola-10 at 5:1 mol ratio showed two breaks in the tensiometry plot (Figure 2F inset). Two breaks in tensiometry were reported²⁰ on the mixed systems of BPHTAB

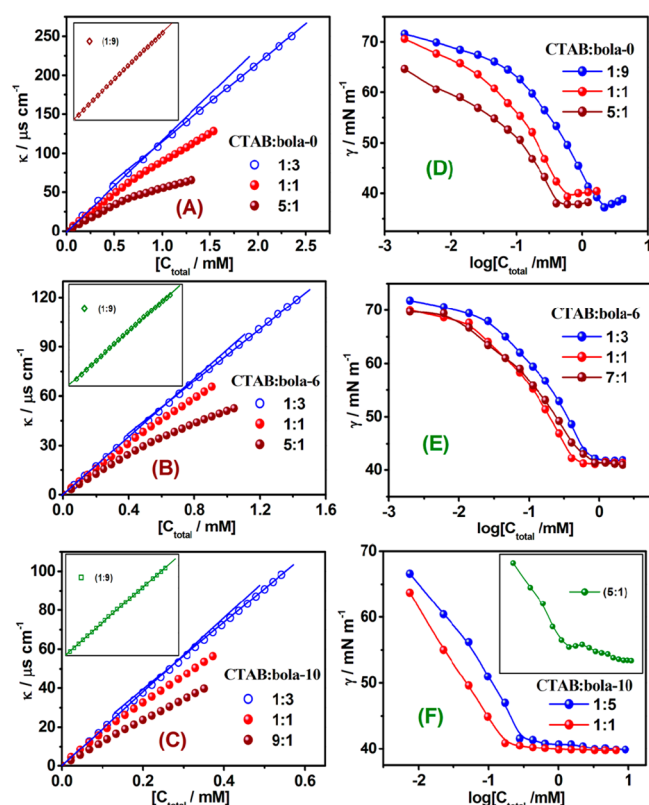


Figure 2. Conductometric and tensiometric profiles of bolas of spacers of 0, 6, and 10 mixed with CTAB at different CTAB:bola mole ratios at 303 K. Insets of (A), (B), and (C) are conductometric plots of 1:9 (CTAB:bola) mole ratio and inset of (F) is the tensiometric plot for 5:1 (CTAB:bola) mole ratio.

(biphenyl-4,4'-bis(oxyhexamethylenetrimethyl-ammonium bromide)) with SDS and $C_9H_{19}COONa$. DLS and SANS studies (subsequently discussed in sections 3.4 and 3.5) could not provide support to the above tensiometric observation in relation to the configuration status in the bulk.

Energetics of micellization of CTAB-bola systems were determined following the procedure described in the literature.³³ The standard Gibbs free energy of micellization (ΔG_m^0) was calculated using β (fraction of counterion bound to micelle),

gas constant (R), and temperature (T) in the relation, $\Delta G_m^0 = (1 + \beta)RT \ln X_{CMC}$, where X_{CMC} is the mole fraction concentration of surfactant at CMC. In the studied systems conductance did not show breaks up to the mole ratio 1:7 ($X_{CTAB} = 0.125$). Systems with $X_{CTAB} = 0.167$ to 1.0 produced β which increased with increasing X_{CTAB} ; with increasing spacer the magnitude of β decreased. Charge neutralization of CTAB micelles by the increasing proportion of bola caused reduction in β , i.e., increase in the micelle ionization degree. The spontaneity of micellization increased with increasing proportion of CTAB in the mixture (i.e., ΔG_m^0 continued to decrease). Spontaneity also increased with increasing spacer length. In Table 1 (main text and also SI Tables 1–5), the CMC values as well as magnitudes of other physicochemical properties for different CTAB-bola electrolyte mixed systems are presented.

In Figure 3, CMC and β are plotted against the spacer number (n) of bola for their mixtures at $X_{CTAB} = 0.167(1:5)$,

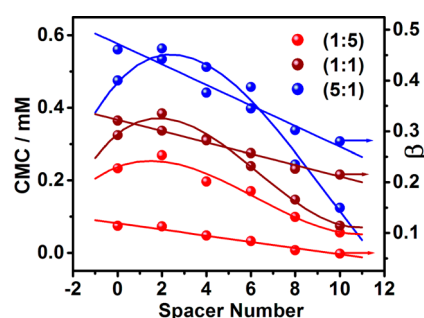


Figure 3. Plot of CMC and β vs spacer number in bola for CTAB-bola mixed system of different ratios 1:5, 1:1, and 5:1 at 303 K.

0.5(1:1), and 0.833(5:1). β linearly decreased with spacer number (correlation coefficient = 0.984, 0.995, and 0.975, respectively). CMC showed a maximum at $n = 2$, and then declined; with n the CMCs fitted to three degree polynomials of the form: $CMC = a_1 + a_2n + a_3n^2 + a_4n^3$; where a_1 , a_2 , a_3 , and a_4 are the constants. Similar results were also found for other ratios (not illustrated). The magnitude of β per spacer in the bola found from the slopes of the lines were 0.01, 0.01, and 0.02 corresponding to X_{CTAB} 0.167, 0.500, and 0.833, respectively; they were nearly equal.

Table 1. CMC, β , $-\Delta G_m^0$, A_{min} , Γ_{max} , and $-\Delta G_{ad}^0$ for Mixed CTAB + bola-6 in Aqueous Medium in Different Mole Ratios at 303 K^a

ratios (CTAB:bola)	X_{CTAB}	CMC/mM			β	$-\Delta G_m^0$	A_{min}	$10^6 \Gamma_{max}$	$-\Delta G_{ad}^0$
		Cond.	ST	Mean					
0:1	0								
1:9	0.1		0.159	0.159			1.12	1.36	
1:7	0.125		0.160	0.160			1.20	1.38	
1:5	0.167	0.168	0.173	0.170	0.084	34.1	1.19	1.39	63.7
1:3	0.25	0.188	0.181	0.184	0.101	34.4	1.04	1.60	60.5
1:1	0.5	0.238	0.240	0.239	0.257	38.4	0.94	1.76	61.8
3:1	0.75	0.399	0.391	0.395	0.316	38.6	0.91	1.83	61.0
5:1	0.833	0.457	0.457	0.457	0.345	39.0	0.87	1.91	60.4
7:1	0.875	0.579	0.579	0.579	0.392	39.5	0.77	2.17	58.2
9:1	0.9	0.641	0.612	0.626	0.459	41.2	0.97	1.72	64.9
1:0	1	0.930	1.020	0.970	0.682	45.6	0.55	3.01	58.4

^a ΔG_m^0 , A_{min} , Γ_{max} , and ΔG_{ad}^0 are expressed in kJ mol^{-1} , $\text{nm}^2/\text{molecule}$, mol m^{-2} , and kJ mol^{-1} , respectively. Their respective standard deviations are ± 4 , ± 6 , ± 5 , $\pm 3\%$. Standard deviations in CMC = $\pm 4\%$, and in β = $\pm 5\%$.

Interestingly, CMC produced by bola-0 with no hydrophobic spacer was lower than bola-2. It was a unique property. We considered that bolas did not form mixed micelles with CTAB; they acted like surface active salts in solution and decreased CMC of CTAB micelles with increasing spacer length. This was supported from the study of Yu et al.³⁸ on the effects of organic salts ($\text{C}_6\text{H}_5\text{COONa}$ and $\text{p-C}_6\text{H}_4(\text{COONa})_2$) on the aggregation of cationic gemini surfactants. They have shown that the hydrophobic inorganic salts were more effective to promote aggregation of geminis than normal inorganic salts. The bola class salt $\text{p-C}_6\text{H}_4(\text{COONa})_2$ promoted aggregate formation through reduction of the electrostatic repulsion among the gemini headgroups because it stayed at the micelle surface rather than penetrating into the hydrophobic core like $\text{C}_6\text{H}_5\text{COONa}$. Similar was our consideration for bolas: they could not penetrate the core because of two oppositely placed ionic headgroups. The “reverse wicket-like” configuration modeled in Figure 4B (II) is discussed in section 3.4. This proposition fitted with the scheme of Yu et al. (scheme 1 lower).³⁸ Amphiphiles with a single hydrophilic ionic headgroup are known to easily penetrate into the hydrophobic core or region to form mixed micelles or microemulsions (and reverse micelles). Amphiphiles with two ionic headgroups as bolas (being more hydrophilic) do not fit in this line. We have been trying with

the bolas to prepare microemulsions, but so far with little success.

3.3. Interfacial Properties of Mixed (CTAB-bola) Systems. Interfacial adsorption of CTAB–bola combinations was computed from the Gibbs adsorption equation.³⁹ Surface excess (Γ_{max}) values at CMC were found from the slopes of the γ vs $\log C$ plots.

$$\Gamma_{\text{max}} = -\frac{1}{2.303rRT} \lim_{C \rightarrow \text{cmc}} \frac{d\gamma}{d \log C} \quad (2)$$

Both CTAB and bolas were surface active; the micelle formation of CTAB was influenced by the bolas, so interfacial adsorption where both species were adsorbed also. The r in eq 2 was composition dependent.⁴⁰ Its value was found from the relation, $r = \sum_i r_i x_i$, where r_i and x_i correspond to the number of species formed from the i -th component and the mole fraction of the component, respectively. Species formed from CTAB in solution by dissociation are two ($\text{CTA}^+ + \text{Br}^-$), and those formed from a bola are three ($^-\text{OOC} - (\text{CH}_2)_n - \text{COO}^- + 2\text{Na}^+$). Hence at 1:1 ratio, $r = 2 \times 0.5 + 3 \times 0.5 = 2.5$, at 5:1, $r = 2 \times 0.833 + 3 \times 0.167 = 2.17$, etc. In getting the slope ($d\gamma/d \log C$), a two-degree polynomial equation of the form $\gamma = a + b \log C + c \log C^2$ was considered whose slope at $C = \text{CMC}$ was used to get Γ_{max} .^{39,41} In many literature reports, arbitrary straight lines are drawn through the CMC point whose slopes are taken to get incorrect Γ_{max} .⁴² The minimum area of exclusion of the surfactant molecules at the air–water interface was calculated from the relation

$$A_{\text{min}} = \frac{10^{18}}{N_A \Gamma_{\text{max}}} \text{nm}^2/\text{molecule} \quad (3)$$

where N_A is the Avogadro number.

The data in Table 1 and also in SI Tables 1–5 show that the A_{min} of CTAB ($0.55 \text{ nm}^2/\text{molecule}$) increased with increasing proportion of bola, and finally at $X_{\text{CTAB}} = 0.1$, A_{min} of the mixed system nearly doubled ($\sim 1.20 \text{ nm}^2/\text{molecule}$). The phenomenon was independent of the size of the bola, which was an interesting observation. The studied bolas did not form micelles but they were surface active. This supported flat orientation of small bolas (up to spacer 4), and higher bolas had “bent” or “wicket-like” conformation.

By comparison of the area per molecule (A_{min}) of “one-headed” $\text{C}_{12}\text{H}_{25}\text{Me}_3\text{N}^+$ ($0.55 \text{ nm}^2/\text{molecule}$), $\text{C}_{12}\text{H}_{25}\text{Bu}_3\text{N}^+$ ($0.73 \text{ nm}^2/\text{molecule}$), with the corresponding “two-headed” bolas, $\text{C}_{12}\text{H}_{25}\text{Me}_6\text{N}^+$ ($1.07 \text{ nm}^2/\text{molecule}$) and $\text{C}_{12}\text{H}_{25}\text{Bu}_6\text{N}^+$ ($1.46 \text{ nm}^2/\text{molecule}$), Menger et al.¹⁵ also suggested a “wicket-like” orientation of bolas at the interface (A_{min} values of “one-headed” species were half the A_{min} values of the “two-headed” bolas). Yan et al.¹⁹ have reported A_{min} values for their

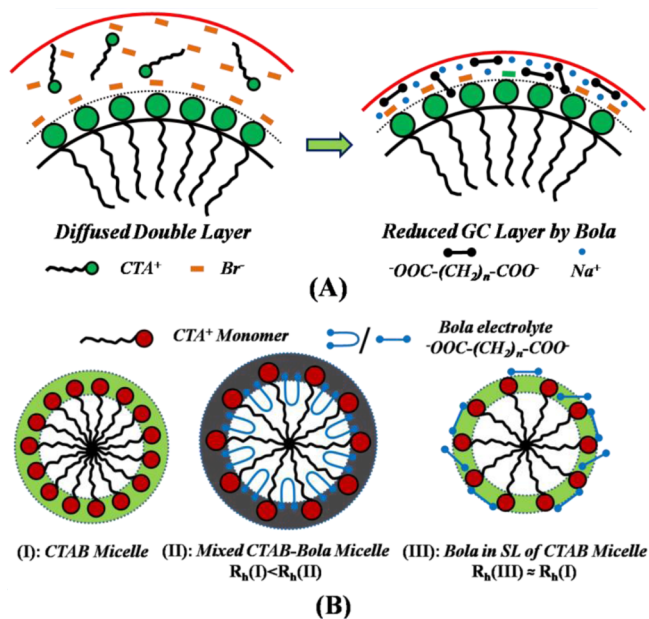


Figure 4. Suggested structures of CTAB micelle with electrical double layer in the absence and presence of bola electrolytes.

Table 2. CMC, β , $-\Delta G_{\text{m}}^0$, A_{min} , Γ_{max} , and $-\Delta G_{\text{ad}}^0$ for (1:1) Mixed CTAB+bola in Aqueous Medium at 303 K^a

systems (CTAB:bola)	CMC/mM			β	$-\Delta G_{\text{m}}^0$	A_{min}	$10^6 \Gamma_{\text{max}}$	$-\Delta G_{\text{ad}}^0$
	Cond.	ST	Mean					
Bola-0	0.371	0.296	0.324	0.321	36.9	0.81	2.04	53.1
Bola-2	0.413	0.356	0.384	0.301	38.3	0.81	1.90	54.2
Bola-4	0.337	0.291	0.314	0.282	38.4	0.84	1.97	53.9
Bola-6	0.238	0.240	0.239	0.257	38.4	0.94	1.76	61.8
Bola-8	0.149	0.146	0.147	0.226	36.8	0.99	1.67	54.9
Bola-10	0.064	0.086	0.075	0.215	40.6	1.18	1.41	47.8

^aUnits and standard deviations of the parameters are as in Table 1.

Table 3. Interfacial Parameters Obtained from Rosen's Mixed Monolayer Model for Three Different Molar Ratios of CTAB:bola at 303 K^a

systems	$(X_{\text{CTAB}}^{\sigma})_{55}$ $(X_{\text{CTAB}}^{\sigma})_{65}$	$(\beta_{\text{R}}^{\sigma})_{55}$ $(\beta_{\text{R}}^{\sigma})_{65}$	$(f_{\text{CTAB}}^{\sigma})_{55}$ $(f_{\text{CTAB}}^{\sigma})_{65}$	$(f_{\text{bola}}^{\sigma})_{55}$ $(f_{\text{bola}}^{\sigma})_{65}$
1:3 ratio				
Bola-6	0.63(0.82)	-8.97(-6.82)	1.02(1.01)	1.16(1.09)
Bola-8	0.67(0.72)	-11.20(-8.69)	1.02(1.02)	1.20(1.16)
Bola-10	0.60(0.60)	-14.45(-16.49)	1.03(1.03)	1.25(1.25)
1:1 ratio				
Bola-6	0.76(0.83)	-9.77(-8.82)	0.087(0.110)	0.087(0.110)
Bola-8	0.69(0.72)	-12.56(-11.85)	0.043(0.052)	0.043(0.052)
Bola-10	0.63(0.68)	-14.28(-11.32)	0.028(0.059)	0.028(0.059)
3:1 ratio				
Bola-6	0.82(0.85)	-9.10(-9.70)	1.11(1.09)	1.01(1.00)
Bola-8	0.73(0.76)	-12.33(-11.79)	1.16(1.14)	1.02(1.02)
Bola-10	0.69(0.66)	-15.70(-13.29)	1.21(1.19)	1.02(1.02)

^aThe interfacial parameters were calculated from the following relations A, B, and C:

$$\frac{(X^{\sigma})^2 \ln(\alpha_1 C_{\text{mix}} / X^{\sigma} C_1^0)}{(1 - X^{\sigma})^2 \ln[(1 - \alpha_1) C_{\text{mix}} / (1 - X^{\sigma}) C_2^0]} = 1 \quad (\text{A})$$

where C_{mix} , C_1^0 , and C_2^0 are the concentrations of the mixture, component 1, and component 2, respectively, at a fixed γ ; α_1 is the stoichiometric mole fraction of component 1 in solution and X^{σ} is its interfacial composition in mole fraction.

$$\beta_{\text{R}}^{\sigma} (\text{interaction parameter}) = \frac{\ln(\alpha_1 C_{\text{mix}} / X^{\sigma} C_1^0)}{(1 - X^{\sigma})^2} \quad (\text{B})$$

$$\begin{aligned} f_1^{\sigma} (\text{activity coefficient of component 1}) \\ &= \exp[\beta_{\text{R}}^{\sigma} (1 - X^{\sigma})^2], \\ &\text{and } f_2^{\sigma} (\text{activity coefficient of component 2}) \\ &= \exp[\beta_{\text{R}}^{\sigma} (X^{\sigma})^2] \end{aligned} \quad (\text{C})$$

Results were iteratively calculated in a computer.

cationic (trimethylammonium) bolas Ia (phenyl-1,4-bis-(oxyhexyltrimethylammonium bromide)), Ib (phenyl-1,4-bis-(oxydecyltrimethylammonium bromide)), and Ic (biphenyl-4,4'-bis-(oxyhexyltrimethylammonium bromide)) as 1.66, 3.67, and 1.76 nm²/molecule, respectively. These values were also reasonably higher in comparison with the A_{min} of a -N⁺Me₃ headgroup (~0.50 nm²/molecule) reported in the literature.⁴³ The bola Ia with $n = 6$ and a phenyl ring in the middle had a CMC = 11 mM, whereas Ib with $n = 10$ and a middle phenyl ring had a CMC = 2.9 mM; Ic with $n = 6$ and a middle diphenyl ring evidenced a CMC = 6.8 mM at 303 K, which indicates that the hydrophobicity of a phenyl ring \cong the hydrophobicity of two methylene groups. The presence of single and double phenyl rings in the middle of the bolas produced CMC although n values were 6 and 10, well below the CMC forming capability ($n \geq 12$) of alkyl chain containing bolas.¹⁹ Mono- and biphenyl rings in the middle added the requisite hydrophobicity to the compounds to form micelles. In Table 2 the above-mentioned physicochemical parameters of herein studied bolas at 1:1 (mol/mol) CTAB:bola ratio are presented. In overall comparison, bola-10 behaved adequately differently with respect to ΔG_{m}^0 and A_{min} from the rest; the differences in the other parameters were small.

Both bola electrolytes and CTAB (although did not form mixed micelles in solution) were simultaneously adsorbed at the air/solution interface; there, they underwent mutual interaction. Surface compositions of the amphiphiles (bola and CTAB) were determined from Rosen's rationale (RR)⁴⁴ and are listed in Table 3. Additionally, the surface activity coefficients of the components and the interaction parameters were also evaluated. The constant levels of surface tension required for the above estimation were arbitrarily chosen at $\gamma = 55$ and 65 mN m⁻¹. The final forms of the relations used are presented in the footnote of the table.

The results in Table 3 revealed that (i) the interfacial composition (IC) of CTAB increased with stoichiometric composition (SC) in the presence of bolas (the IC values > SC values), i.e., for bolas, IC values < SC values; and (ii) the increasing presence of hydrophobicity of bolas increased its IC, and caused a decrease of IC of CTAB. The IC vs SC plots for bola-6, 8, and 10 are presented in Figure SI 1(A, B).

In the Rosen mixed monolayer treatment, only bola-6, bola-8, and bola-10 were considered. Lower bolas with spacers 0, 2, and 4 were very weakly surface active and comparison at $\gamma = 55$ and 65 mN m⁻¹ was not possible. In all proportions of CTAB and bola, mole fractions of the components at the air/water

interface were different from the stoichiometric compositions in solution. Thus, $[X_{\text{CTAB}}]_{\text{monolayer}}^{3:1} \approx [X_{\text{CTAB}}]_{\text{soln}}^{3:1}$, $[X_{\text{CTAB}}]_{\text{monolayer}}^{1:1} > [X_{\text{CTAB}}]_{\text{soln}}^{1:1}$, and $[X_{\text{CTAB}}]_{\text{monolayer}}^{1:3} \gg [X_{\text{CTAB}}]_{\text{soln}}^{1:3}$. The corresponding compositions of bolas in the monolayer and in solution followed from above. It was found that with increasing spacer length, the proportion of CTAB at the interface decreased. Higher bolas were surface active enough to compete with CTAB in the formation of Gibbs monolayer (GM); increasing spacer length increased the proportion of bola in the GM, but the fraction of CTAB always remained $>$ bola. There was no marked difference between the results found from the two γ values 55 and 65 mN m⁻¹. The activity coefficients of both components in each set were nearly equivalent, but their magnitudes for the mole ratios 3:1 and 1:3 were like ideal mixtures, which for 1:1 mol ratio were highly nonideal. The interaction parameters β_R^σ were all negative with fairly high values. The components showed strong synergistic interaction, which increased with increasing spacer length in the bola. Average values of β_R^σ for bola-6, bola-8, and bola-10 were -9.3 , -12.0 , and -14.8 , respectively, at 303 K. In a previous study,¹⁷ we presented interactions of different types of bolas with oppositely charged conventional surfactants like SDS and CTAB. Since they formed mixed micelles, both Rubing's regular solution theory and Rosen's model were used to get information in the solution and at the interface. There, interactions of bola ($\text{Br}^-\text{Me}_3\text{N}^+-(\text{CH}_2)_{10}-\text{COO}^-\text{Na}^+$) with CTAB and SDS were also synergistic with fairly large β_R^σ values -17.0 and -6.72 with CTAB and SDS, respectively. At 1:1 mol ratio, the interfacial composition of CTAB or SDS with respect to the solution was $[X_{\text{CTAB}} \text{ or } X_{\text{SDS}}]_{\text{monolayer}}^{1:1} > [X_{\text{CTAB}} \text{ or } X_{\text{SDS}}]_{\text{soln}}^{1:1}$. The activity coefficients at 1:1 mol ratio were small; $[f_{\text{bola}}]_{\text{monolayer}}^\sigma \ll [f_{\text{CTAB}} \text{ or } f_{\text{SDS}}]_{\text{monolayer}}^\sigma$ for both pairs.

3.4. Zeta Potential (Electrical Double Layer Behavior) And Hydrodynamic Radius. Bola was expected to affect the size and charge of the CTAB micelle and consequently its zeta potential. DLS measurements provided the micelle size and ζ potential. The measured ζ -potential of the CTAB micelles was $+32.9$ mV at 303 K. Addition of bola with different spacers reduced ζ from $+32.9$ to $+4.65$ mV. The results at two mixing ratios, 1:1 and 2:1 (mol/mol) of CTAB:bola at an overall concentration of 10 mM, are presented in Table 4 (a graphical representation is given in Supporting Information Figure SI 2).

An initially large depression of ζ of CTAB micelle by oxalate followed by a continuous moderate decline over and above that of oxalate by higher bolas was observed. The ζ -potential of 1:1 mol proportion of CTAB:bola was higher than that of 2:1 excepting bola-10. At 1:1 molar proportion, the concentration of the micelle was lower than that at 2:1. Stoichiometrically, in the first CTAB molecules were expected to be totally neutralized by one equivalent of bola, and one equivalent of non-neutralized carboxylate anion in bola remained free. In the second, total charge neutralization with a neutral condition was the expectation. Both were not found: at 1:1 proportion ζ -potential was considerably reduced compared to pure CTAB micelle, and at 2:1, it was reduced further but did not become zero or very small. ζ decreased with increased spacer length; the Stern-layer (in the electrical double layer of CTAB micelles) did not accommodate enough bolas for steric and other accommodative restrictions. By consideration of $\zeta \propto$ surface charge (net charge of the diffuse or Gouy–Chapman double layer), the % neutralization of charge relative to CTAB micelle is tabulated in column 6 (Table 4) as an overall estimation (see footnote of the table). 60–90% neutralization of charge with a

Table 4. Physicochemical Parameters of Aggregates of CTAB+Bola Mixture from DLS and Anisotropy Measurement at 303 K^a at 10 mM

systems	CTAB:bola	r_{ss}	R_h / nm	zeta potential ^b (ζ /mV)	% charge neutralized
CTAB	-	0.069	2.69	32.9	0
Bola-0	1:1	0.070	2.74	10.2	69
	2:1	0.071	2.66	12.4	62
Bola-2	1:1	0.066	2.78	16.1	51
	2:1	0.064	2.84	11.9	64
Bola-4	1:1	0.066	2.50	12.7	61
	2:1	0.067	2.62	10.6	68
Bola-6	1:1	0.064	2.80	9.46	71
	2:1	0.065	2.36	8.60	74
Bola-8	1:1	0.062	2.81	6.81	79
	2:1	0.062	2.51	5.32	84
Bola-10	1:1	0.064	2.69	3.38	90
	2:1	0.066	2.81	4.65	86

^a $100(\zeta_{\text{CTAB}} - \zeta_{\text{bola}})/\zeta_{\text{CTAB}}$. ^bStandard deviation in r_{ss} , R_h , and ζ are ± 2 , ± 6 , and $\pm 4\%$, respectively.

few minor inconsistencies (experimental artifacts) was observed. The degree of neutralization of the double layer charge increased with increasing molecular size (length) of the bolas. Higher bolas by their mass and mobility restrictions had greater probability of residence in the electrical double layer. Interestingly, the average R_h values of the micelles at both mole ratios 1:1 and 2:1 were close (the values were independent of the spacer length; the averages at 1:1 and 2:1 mol ratios were 2.72 and 2.62 nm, respectively). They were closely comparable with those of pure CTAB micelle ($R_h = 2.69$ nm), which potentially supported the absence of mixed micelles.

Therefore, bolaforms did not form mixed micelles in solution; they influenced the interfacial adsorption, i.e., Γ_{max} and hence A_{min} . Formation of mixed micelles would expect to expand the micelle size for their residence in the micelle phase. Weak influence of bolas on R_h at both 1:1 and 2:1 CTAB:bola mole ratios suggested their noninclusion in the micelle interior. They accumulated in the diffuse Gouy–Chapman double layer, and reduced its thickness to make ζ decline with slight variation in R_h . It is pictorially presented in Figure 4A.

Figure 4B is a comparative presentation of CTAB micelle and its bola interacted form together with a hypothetical assembly containing bolas in a “reverse wicket-like” conformation placed in the micelle interior to make the mixed micelle expand. According to the results and the above discussion, model (II) in Figure 4B is impracticable whereas model (I) \equiv model (III) (with respect to size). Model (III) is also equivalent to the scheme 1 (lower) of Yu et al.³⁸ Conclusion section provides additional reasoning against the formation of mixed micelles between bola and CTAB.

3.5. Microstructures of (CTAB– and DTAB–Bola) Mixed Systems. Quantitative estimation of aggregate morphology, N_{agg} , micelle charge can be obtained from model fitting of SANS spectra. In addition to CTAB in the SANS experiments we have also studied DTAB (dodecyltrimethylammonium bromide) to get additional information on a lower homologue of the alkyl trimethylammonium bromide series. Both CTAB and DTAB aggregates with or without bolas were modeled as charged prolate ellipsoids interacting through a screened Coulomb potential.^{29,45} SANS data were analyzed using this model wherein the differential scattering cross

section per unit volume ($d\Sigma/d\Omega$) as a function of scattering vector q can be written as

$$\frac{d\Sigma}{d\Omega} = \bar{n}(\rho_m - \rho_s)^2 V^2 [\langle F(\mathbf{q})^2 \rangle + \langle F(\mathbf{q}) \rangle^2 (S(\mathbf{q}) - 1)] + B \quad (4)$$

where \bar{n} denotes the number density of micelles, ρ_m and ρ_s are the scattering length densities of the micelle and the solvent, respectively, and V is the volume. $F(\mathbf{q})$ is the single particle form factor, and $S(\mathbf{q})$ is the interparticle structure factor. B is a constant term which represents the incoherent scattering background coming mainly from the hydrogen atoms present in the sample, and $F(\mathbf{q})$ is calculated using the relations:

$$F(\mathbf{q}, \mu) = \frac{3(\sin x - x \cos x)}{x^3} \quad (5)$$

$$x = q[a^2\mu^2 + b^2(1 - \mu^2)]^{1/2} \quad (6)$$

where a and b are the semimajor and semiminor axes of an ellipsoid micelle ($a > b = c$), respectively, and μ is the cosine of the angle between the directions of a and the wave vector q . The interparticle structure factor $S(\mathbf{q})$ has been calculated using expressions derived by Hayter and Penfold from the Ornstein–Zernike equation making the rescaled mean spherical approximation (RMSA).^{34,46} The fractional charges of the semimajor and semiminor axes are used as the variables in the fit. For a better fit, a polydispersity in the semimajor axis is necessary, and is considered using the Schultz distribution;^{47,48} a polydispersity parameter $z = 35$ was used in the process. The micelle aggregation number was calculated from the relation $N_{\text{agg}} = 4\pi b a^2 / v$ where v is the surfactant monomer volume (found from Tanford formula⁴⁹). Experimental data were found to fit well with the model: the derived parameters from the fit (presented in Figure 5) are tabulated in Table 5. Recently, from

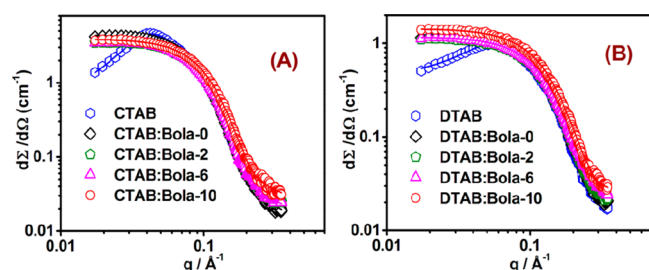


Figure 5. SANS spectra for (A) pure CTAB; (B) DTAB and mixtures with different bola electrolytes at 303 K (solid lines show the fits to the data). [CTAB] = 50 mM and [DTAB] = 50 mM.

SANS measurements Liu et al.⁵⁰ reported that, unlike alkyltrimethylammonium halides, micelles were small and spherical with hydrolyzable counterions of all valences (phosphate, oxalate, and carbonate), and remain spherical even in the presence of added salt by way of strong binding that “prevents the screening of repulsions between adjacent headgroups necessary for sphere–cylinder transformation”. In the present study, 1:1 mol ratio of CTAB or DTAB and bolas (0, 2, 6, 10) was used, and SANS results were fitted to the prolate geometry^{36,47} of the alkyltrimethylammonium bromide micelles. The presence of sufficient Br^- (50 mM) and bola ions (100 mM) in the system prevented spherical geometry of the micelles.

SANS studies on the characterization of CTAB–bola mixed systems at 1:1 (mol/mol) mixtures at 50:50 mM (much higher

Table 5. Parameters Obtained from the SANS Analysis for 1:1 Mixtures of CTAB, DTAB, and Different Bola Electrolytes at 303 K^{a,b}

systems	aggregation number (N_{agg})	semimajor axis ($a/\text{\AA}$)	semiminor axis ($b/\text{\AA}$)	fractional charge (α)
CTAB	152	42.58	21.84	0.14
CTAB:Bola-0	142	42.37	21.17	0.13
CTAB:Bola-2	137	40.90	21.17	0.13
CTAB:Bola-6	118	39.07	20.11	0.12
CTAB:Bola-10	97	34.85	19.25	0.11
DTAB	63	26.45	15.98	0.27
DTAB:Bola-0	61	28.67	15.17	0.18
DTAB:Bola-2	61	27.32	15.51	0.18
DTAB:Bola-6	57	26.21	15.27	0.15
DTAB:Bola-10	52	26.83	14.47	0.11

^aConcentration of all CTAB and DTAB were 50 mM. ^bStandard deviation in N_{agg} , a , b , and α are ± 6 , ± 3 , ± 3 , and $\pm 2\%$, respectively.

than the CMC of CTAB) produced some interesting results (Figure 5). It was found that mixed species of CTAB and bola were not formed (since all the spectra nicely overlapped with the parent component). The same was true for DTAB. The derived results are presented in Table 5.

N_{agg} , a , b , and α of CTAB micelles declined with interaction with bolas with increasing number of the spacer. The dependence was nicely linear with spacer number (Figure SI 3). Electrostatic interactions between the cationic CTAB and the anionic bola molecules helped easier formation of micelles. Micelle size decreased by lowering the solvent polarity by the bolas (solvophobic effect), like nonpolar water-miscible solvents in general.³³ Empirical relation of the following type correlated the results.

Thus,

$$N_{\text{agg}}^{\text{obs}} = N_{\text{agg}}^{\text{CTAB}} - 5m(\text{COO}^-) - 4.5p(\text{CH}_2) \quad (7)$$

where $m(\text{COO}^-)$ and $p(\text{CH}_2)$ represent the number of carboxylate and methylene groups present in the bolaform, respectively.

The SANS results of DTAB–bola at 1:1 mol ratio are also presented in Figure 5B and Table 5. N_{agg} values found for DTAB were smaller than CTAB and reasonably tallied with literature values (of course, because of higher concentration of the surfactants required in SANS experiments, N_{agg} were on the higher side⁵¹). N_{agg} also decreased with increasing spacer length in bola; a 36% decrease in N_{agg} of CTAB micelle and 16% of DTAB micelle were caused by bola-10. The effect of spacer length of bola on the semimajor axis of micelles was appreciable on CTAB and moderate on DTAB, whereas the fraction of the dissociated counterions increased in both cases. Smaller micelles with lesser charge density increased counterion dissociation. A SANS study of the effect of neutral sugars (50 mM) on nonionic surfactant $\text{C}_{12}\text{E}_{10}$ showed high N_{agg} . Addition of sugar increased as well as decreased N_{agg} depending on the concentration. The semiminor axis remained essentially constant, but the semimajor axis changed.⁵² The correlation found for CTAB (eq 7) was not observed for DTAB. The above results suggested a preference of bolas near the cationic micelles to influence the overall charge and the potential of the electrical double layer. The fractional charge of pure CTAB micelle at higher concentration was 0.14, which was reduced by bola-0 (a salt without a spacer) to 0.13, and was reduced onward by bolas with increasing spacers up to 0.11 by bola-10. The amphiphilic

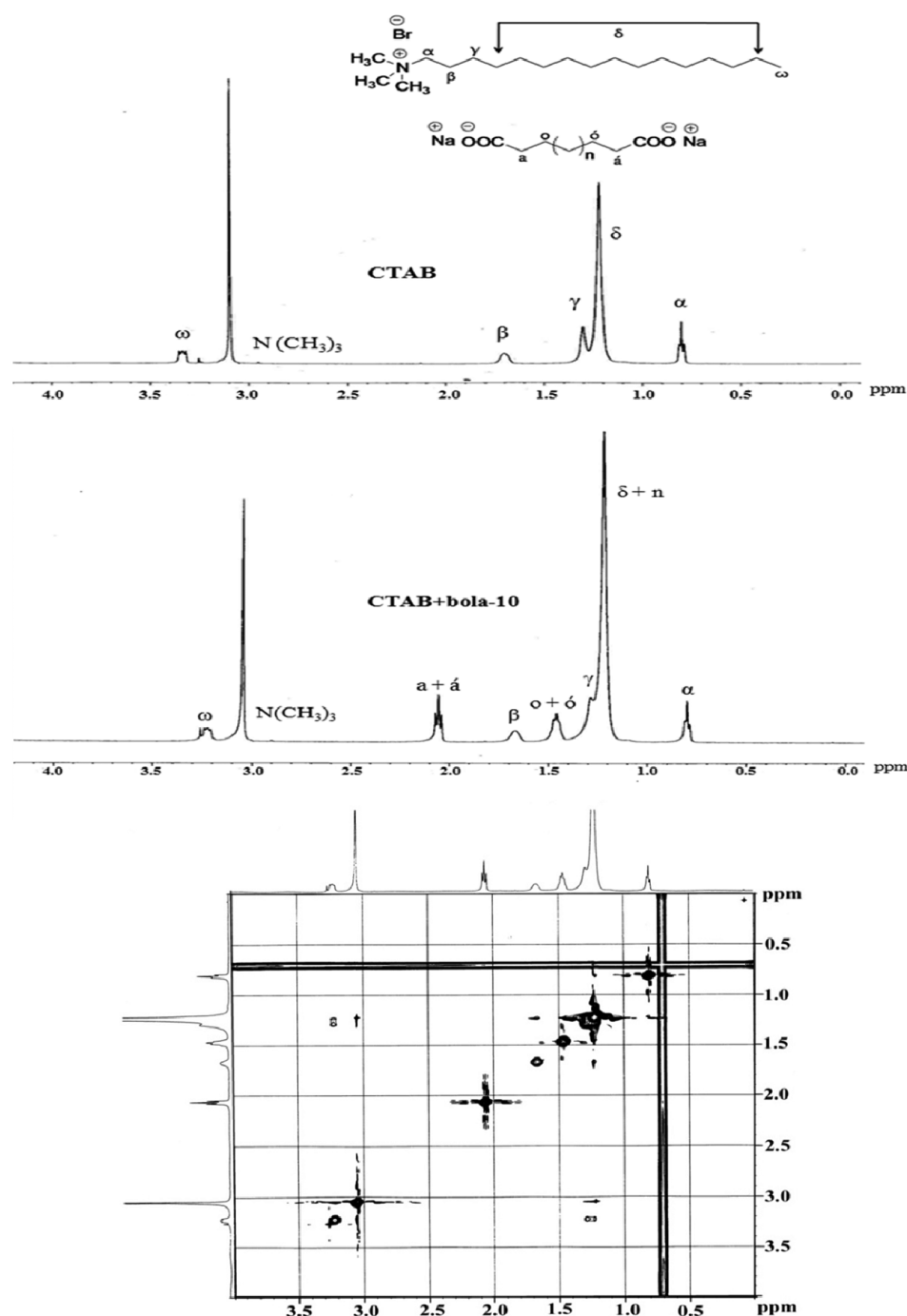


Figure 6. ^1H NMR spectra (top) of 10 mM of CTAB, and (middle) 10 mM 1:1 mol ratio of CTAB:bola-10 system. 2D-NOESY spectra (bottom) of CTAB-bola-10 mixed system at 1:1 molar ratio in D_2O .

bola electrolytes were accommodated more in the double layer to make the observed continued reduction. A similar decrease in the surface charge of micelles by bolas with increasing spacers was also found from zeta potential measurements.

The ionization degrees of the counterions at the aggregation points (0.08–0.32 mM) of the globular micelles at 1:1 (mol/mol) composition were found to be 0.68–0.78 (Table 2), whereas those found from SANS at concentrations >200-fold are only 0.11–0.14. At swamping concentrations, the anionic bola electrolytes caused the counterions to be much less dissociated from the prolate micelles. The counterion dissociation degree found from zeta potential measurements at 50-fold concen-

tration was in the range of 0.20–0.40. Results by SANS and electrokinetic measurements are nearly comparable; lower concentration in the latter yielded 10–30% higher degree of dissociation.

3.6. NMR Spectroscopy. NMR is a powerful and reliable method for investigating surfactant aggregates.^{53,54} Both 1D and 2D NMR techniques can be successfully applied to study static (micelle size and shape, degree of association, structure) as well as dynamic (molecular mobility, kinetics of micelle formation) properties of surfactant systems. 2D-NOESY measurement is a potential way to measure dipolar interactions between protons for understanding three-dimensional structure.^{55,56}

NMR study can lend information of interactions in micelle, reverse micelle, and microemulsion systems;^{57,58} employment of NMR method to explore mixed surfactant systems has also been reported.⁵⁹ ¹H-NMR experiments were performed to understand the intermolecular interaction in the mixed CTAB–bola system. Results on their mixed solution at 1:1 molar ratio of CTAB:Bola-10 at 10 mM are documented in Figure 6.

Proton signals of the system did not show any chemical shift compared to their individual proton signals in the pure state. The existence of a noninteracting individual structure in the mixed CTAB–bola system was evidenced. 2D-NOESY experiments were then performed to get information on the interaction between protons of the herein mixed systems. As per structural identification (top of Figure 6), information on the interaction of δ -H of CTAB and n -H of bola with other protons in the mixed system was restricted because of overlap of these resonance peaks, and no cross peaks in 2D-NOESY spectra of CTAB–bola mixed systems at 1:1 mol ratio was observed (bottom of Figure 6). We have thus inferred non-incorporation of bolas in the CTAB micelles. The surface active bola electrolytes coexisted and interacted with CTAB at the air/solution interface and did not participate in the formation of mixed micelles.

3.7. Possibility of Vesicle Formation. Dimeric surfactants, geminis, dimeric lipids, and bolaamphiphiles are used with monomeric amphiphiles to form vesicular species in aqueous medium. Thus, vesicular aggregation of dicarboxylates (with spacer numbers 8 and 10) by interaction with CTAB might be a possibility. We have studied the fluorescence anisotropy (r_{ss}) of DPH (1,6-diphenyl-1,3,5-hexatriene) probe in the bola–CTAB mixtures of 1:1 and 1:2 molar ratios. The nonpolar DPH molecule became solubilized in the nonpolar (hydrocarbon) part of the aggregates wherein the rotational diffusion was affected, and hence the fluorescence anisotropy (r_{ss}) was also affected. It is known that for micelles the r_{ss} values are <0.14 , whereas for bilayer aggregates or vesicles $r_{ss} > 0.14$.⁶⁰ Therefore, the r_{ss} values can be used for understanding the nature of the aggregates, micelles, or vesicle. In Table 4, column 3, the r_{ss} values of the bola–CTAB interacted products are presented. The values fall in the range of 0.062–0.071 and are <0.14 . Hence, the assemblies are micelles, not vesicles. For more support, dialysis of water-soluble dye Rhodamine 6G (R6G) taken in the bola–CTAB mixed systems at 1:1 and 1:2 molar ratio is done against the same mixed solutions of bola and CTAB but without dye. In the case of vesicles, the dye entrapped in the interior or core aqueous solution should not pass out of the membrane; only the dye present in the outside solution would come into the dialyzed solution. Thus, the absorbance and fluorescence intensities should decrease for vesicles and will become zero for micelles. The latter was observed in our experiments. The fluorescence anisotropy experimental findings were corroborated. Another single but potential test could be the packing parameters of the produced species. Such calculations and the results are presented in the Supporting Information. All the values were <0.33 signifying the presence of micelles, not bilayers or vesicles, for which P_c should be >0.5 .

CONCLUSION

The studied surface active bolaforms do not self-aggregate in aqueous medium. Those with spacer number ≤ 4 lie flat at the interface, and the rest having spacers ≥ 4 –10 assume “wicket-like” conformation (their $A_{\min} \equiv 2A_{\min}$ of CTAB). The CMC of

CTAB is reduced by the bolas like salts; additionally, by their nonpolarity the aggregation number of CTAB micelles is reduced. The bolas are considered as “amphiphilic electrolytes”. Two ionic headgroups restrict them to penetrate into the CTAB micelles in contrast with amphiphiles having a single headgroup that can insert the nonpolar tail into the micelle core to form mixed entities. This is corroborated by our scant success in preparing microemulsions using bolas of varied spacer lengths. Yu et al.³⁸ also proposed the same reason for the penetration of C_6H_5COONa into the core of cationic micelles of gemini surfactants, for which the bola-like species $p-C_6H_4(COONa)_2$ could not, and remained in the peripheral region. Further, binary surfactants forming mixed micelles always cause a decrease in the CMC_{mix} with increasing proportion of the lower CMC forming component in the composition. This is reversed with increasing proportion of the higher CMC forming component.³ In the studied bola–CTAB mixture, with increasing proportion of bola the CMC of the mixed system decreases. By the above rationale, the increase for the CMC of the bola (if any) should be much higher than that of CTAB. This is the physicochemical confirmation that the studied bolas do not form mixed micelles (they act like electrolytes and continuously decrease the CMC of CTAB). In this context, the possibility of bilayer type vesicular aggregation between dicarboxylates (with spacer numbers 8 and 10) and alkyltrimethyl ammonium salts like CTAB has been examined. The studied bolas (dicarboxylates with spacer 8 and 10) did not form either mixed micelles or bilayer aggregates upon interaction with CTAB. The calculation of packing parameter, determination of DPH anisotropy, and dialysis of R6G dye and DLS studies unequivocally supported the formation of micelles, not vesicles, of bola–CTAB interacting products in solution.

At the air/water interface, the bola and CTAB undergo synergistic interaction. At different mixing ratios, the relative interfacial concentration of CTAB is higher than that of bola. At a fixed mixing ratio, the relative proportion of the latter at the interface increases with the length of its spacer. SANS study supports prolate geometry of CTAB and DTAB micelles. Effect of bolas on the size and charge of CTAB micelles is more prominent than that of DTAB. A much higher concentration of $[CTAB + bola] = 50 \text{ mM}$ (at 1:1 mol/mol) in SANS experiments makes the ionization degree of the prolate micelles 10–15%, which from zeta potential measurements (at $[CTAB + bola] = 10 \text{ mM}$) is 20–40%. At CMC points (0.08–0.32 mM), the ionization degrees are expectedly much higher, 68–78%. The concentration of the amphiphilic electrolytes has an effect on the ionization degree of the formed CTAB micelles.

ASSOCIATED CONTENT

Supporting Information

Table (SI 1–SI 5) of various physicochemical parameters of CTAB with bola-0, 2, 4, 8, and 10. Dependence of IC (interfacial composition) on SC (stoichiometric composition) of mixed CTAB–bola systems at 303 K is presented in Figure SI 1. Figure SI 2 illustrates dependence of zeta potential on spacer number of bola at 1:1, 2:1 (CTAB:bola). Figure SI 3 depicts the variation of SANS parameters with spacer number of bolas in CTAB–bola mixed systems. Text SIT presents calculation of packing parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Phone: +91-33-2414-6411; Fax: +91-33-2414-6266; E-mail: spmcss@yahoo.com.

Notes

The authors declare no competing financial interest.

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