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Self-Aggregation of Synthesized Novel Bolaforms and Their Mixtures with Sodium Dodecyl Sulfate (SDS) and Cetyltrimethylammonium Bromide (CTAB) in Aqueous Medium

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Bolaforms B_1, B_2, and B_3 of the formulas, $Br^-Me_3N^+(CH_2)_{10}N^+Me_3Br^-$, $Br^-Me_3N^+(CH_2)_{10}OH$, and $Br^-Me_3N^+(CH_2)_{10}COO^-Na^+$, respectively, were synthesized, and their properties in the bulk as well as at the air/aqueous NaBr (10 mM) solution interface have been studied. Their interactions with sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) also have been investigated. Tensiometry, conductometry, spectrophotometry, and microcalorimetry techniques were used for characterization and estimation. Both pure bolaforms and their mixtures with SDS and CTAB have been found to self-aggregate, forming micelles in solution. The mixed systems of bolaform and SDS have been observed to form both micelles and vesicles. Their mutual interactions were synergistic, which at the interface was more spontaneous than in the bulk. The interfacial and bulk compositions of the mixed binary systems (bolaform and SDS or CTAB) with their associated interaction parameters have been estimated from the Rosen interaction model and the regular solution theory of Rubingh, respectively. The formed vesicles have been found to entrap the water-soluble dye, bromophenol blue, and the dye solubilized vesicles of B_1−SDS and B_2−SDS completely eluted out of the sephadex column proving their formation. A rough estimation of the size and polydispersity index of the formed micelles and vesicles has been made from DLS measurements.

Introduction

Bolaamphiphiles/bolaforms (or simply bolas) consist of a hydrophobic chain with two hydrophilic head groups at its extremities.[1,2] Due to their special chemical structure, they are capable of self-organizing themselves in an aqueous/aquo-salt environment to form spheres, disks, large cylinders, monolamellar membranes, vesicles,[3] etc. The morphology of the aggregates is largely dependent on (i) the length of the spacer (hydrophobic chain joining the two polar head groups in the molecule) and (ii) its rigidity/flexibility.[4] The presence of a long spacer leads to a micelle because of easier folding, whereas short spacers lead to vesicle formation.[5] Further, the presence of a foreign substance like salt, sugar, etc. in solution also affects the micelle formation.

The bolaforms can mimic the lipids of the cytoplasmic membranes of the archaebacteria that can cope with extreme conditions[6,7] (such as high temperature, pressure, pH, etc.). A literature survey reveals that scientists have been trying to synthesize vesicle forming lipid anlogues.[5,6] It is considered that the mixed bolaform monolayers can be used as model membrane mimetic systems.[8,9] Because of the slower rate of fusion of their monolamellar membranes, bolaforms are considered useful in pharmaceutical preparation of liposomes, and it is already in practice.[10] Uses of anchored bolaforms on smooth solid surfaces are gaining attention where one headgroup remains attached to the surfaces of electrodes, polyelectrolytes, nanoparticles, etc., and the other end functions for solubilization and/or interaction.[11] They may also produce mesoporous structures.[12] More recently, scientists are using bolaforms for extraction of metal ions,[13] to induce ion-pair formation in aqueous solution,[14] and as photosensitive molecules.[15]

In the last two decades, model archaeal lipid molecules have been synthesized and studied.[16−19] The synthesis of bolaforms, with two ammonium head groups, and a single hydrophobic chain has been fairly explored.[16−20] Their tensiometric behaviors and spectral features in aqueous medium have suggested that bolaforms with a spacer of less than 12 methylene[21,22] groups behave as simple electrolytes in aqueous solution whereas those with spacers ≥16 methylene groups generally form micelles.[23,24] Usually, bolaforms with double hydrocarbon chains can easily form globular vesicles in aqueous solution.[20] Vesicle formation by single chain bolaforms has been also reported.[25]

Along with single bolaform systems, their mixed systems with conventional surfactants have attracted the attention of scientists.[16,26−29] Vesicle formation of the mixed systems of bolaforms and conventional surfactants of similar charges has been reported.[29] However, studies on the mixed systems of bolaforms and oppositely charged conventional surfactants are still limited.[16,26] It is known that the conventional ion-pair amphiphiles (IPA) or catanionics (formed between two oppositely charged surfactants) have very low solubility, and they easily form bilayer vesicles.[30] Vesicles in aqueous solutions have importance in the areas of fundamental biophysical chemistry and industries;[27,28] they have application prospects in pharmaceutics, catalysis, microreactors,[31,32] etc. Compared to the natural

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(lipid) and synthetic vesicles (composed of conventional catanionic surfactants), the pure catanionic and mixed bolaform vesicles are more advantageous because they form easily and are very stable.[30,33]

In this study, we report synthesis and interfacial behaviors of three bolaforms having different head groups with identical spacer structures. They are decane-1,10-bis(trimethylammonium bromide) (B_1), *N*-(10-hydroxydecyl)-*N,N,N*-trimethlyammonium bromide (B_2), and *N*-(10-carboxydecyl)-*N,N,N*-trimethylammonium bromide (B_3). The physicochemical properties of these bolaforms and their mixed systems with sodium dodecyl sulfate (SDS) as well as with cetyltrimethylammonium bromide (CTAB) at the air/solution interface and in the bulk (in salt solution) have been studied and discussed. It may be mentioned that this type of bolaform has been rarely studied in the past.[22] With ten methylene spacer groups in the molecules they have been found to self-aggregate in aqueous solution, preferably in salt (NaBr) solution. Their interacted products with the conventional surfactants SDS and CTAB can also form vesicles in addition to micelles.

Experimental Section

Materials. SDS (99%) and CTAB (99%) were products of Sigma and used as received. $C_{10}TAB$ (decyltrimethylammonium bromide) was a 99% pure product of Alfa Aeser (USA). 10-bromodecanol, 11-bromoundecanoic acid, and 1,6-diphenyl-1,3,5-hexatriene (DPH) were purchased from Sigma, Fluka, and Hi Media, respectively. Tetrahydrofuran (THF, GLC purity >99.9%), trimethylamine, and ethyl acetate were obtained from Spectrochem (India). Bromophenol blue, $Na_2S_2O_3$, HgO, NaBr, hexane, CCl_4, MeOH, and EtOH were analytical grade products from SRL (India).

Synthesis of the Bolaforms. 1. B_1 [$Br^-Me_3N^+-(CH_2)_{10}-N^+Me_3Br^-$]. A 250 mL three-necked round-bottom (RB) flask (wrapped with aluminum foil to exclude light) was fitted with a mechanical stirrer and a reflux condenser. A 28.3 mmol sample of HgO was suspended in 100 mL of freshly dried CCl_4 through a pressure equalizer funnel, to it was added 37.7 mmol of 11-bromoundecanoic acid, and the mixture was heated to reflux at 388 K for 0.5 h. After the reflux, 42.2 mmol of Br_2 in 75 mL of CCl_4 was added dropwise for 15 min to the mixture. Another neck of the RB flask was fitted with a glass tube that was immersed in a beaker containing 10% (w/v) $Na_2S_2O_3$. After the reaction, the mixture was cooled in an ice-bath resulting in precipitation and the cooling was continued for 30 min. The material was filtered and the reddish filtrate was vacuum distilled at 453 K, resulting in the formation of a black-colored 1,10-dibromodecane solution. Freshly prepared trimethylamine was added to 28.7 mmol of the 1,10-dibromodecane in a 100 mL RB flask and stirred for 4 h. TLC performed in 10% ethyl acetate in hexane, and the product appeared at $0.7R_f$. The material was concentrated and dried under vacuum. The obtained decane-1,10-bis(trimethylammonium bromide) was crystallized from methanol/ether and filtered and dried. The overall yield was 20 mmol (~51%).

2. B_2 [$Br^-Me_3N^+-(CH_2)_{10}-OH$]. A 10 mmol sample of 10-bromodecanol was taken in a test tube and to it was added freshly prepared trimethyl amine. The tube was then sealed and heated at 313 K for 12 h. The resulting white precipitate was washed with hexane and crystallized from methanol/ether. The yield of the product *N*-(10-hydroxydecyl)-*N,N,N*-trimethylammonium bromide was 8.7 mmol (~87%).

3. B_3 [$Br^-Me_3N^+-(CH_2)_{10}-COO^-Na^+$]. A 11.3 mmol sample of 11-bromoundecanoic acid was taken in a test tube, and to it was added freshly prepared trimethyl amine. The test tube was sealed and then heated at ~323 K for 12 h. The insoluble product was separated by filtration, washed with hexane, and then dissolved in water. The formed acidic solution was then neutralized by NaOH addition. It was then lyophilized to obtain the desired white product of *N*-(10-carboxydecyl)-*N,N,N*-trimethylammonium bromide. The product yield was 9 mmol (~80%).

Characterization of Bolaforms. This section comprises spectroscopic, NMR, mass spectral, and elemental analytical results for characterization of the synthesized bolaforms.

B_1. ^1H NMR (300 MHz, D_2O): δ/ppm = 3.12−3.18 (m, 4H), 2.99 (s, 18H), 1.62 (br, 4H), 1.19 (br, 12H). Anal. Calcd for $C_{16}H_{38}Br_2N_2$ (2 mol % crystal water): C, 42.30; H, 9.32; N, 6.17. Found: C, 42.05; H, 9.01; N, 6.03. ESI-MS: *m/z*: 258.2383 (M^+), *m/z* (calculated): 258.3024 (M^+).

B_2. ^1H NMR (300 MHz, D_2O): δ/ppm = 3.49−3.54 (t, 2H), 3.19−3.25 (m, 2H), 3.02 (s, 9H), 1.69−1.72 (br, 2H), 1.44−1.48 (m, 2H), 1.23−1.28 (br, 12H). Anal. Calcd for $C_{13}H_{30}BrNO$ (1.33 mol % crystal water): C, 48.75; H, 10.28; N, 4.37. Found: C, 48.56; H, 9.64; N, 4.41. ESI-MS: *m/z*: 216.1716 (M^+), *m/z* (calculated): 216.2232 (M^+).

B_3. ^1H NMR (300 MHz, D_2O): δ/ppm = 3.08−3.14 (m, 2H), 2.91 (s, 9H), 1.98−2.03 (t, 2H), 1.59−1.62 (br, 2H), 1.34−1.38 (m, 2H), 1.12−1.17 (br, 12H). Anal. Calcd for $C_{14}H_{29}BrNNaO_2$ (4 mol % crystal water): C, 40.19; H, 8.91; N, 3.35. Found: C, 41.31; H, 7.83; N, 3.16. ESI-MS: *m/z*: 244.1164 $[M - Na^+ - Br^- + 1]^+$, *m/z* (calculated): 243.2198 $(M - Na^+ - Br^-)$.

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

Preparation of Catanionic Solution. Stock solutions of bolaforms, SDS and CTAB were prepared in doubly distilled water (specific conductance, $\kappa = 2-4\ \mu S\ cm^{-1}$ at 298 K). The bolaform−SDS or bolaform−CTAB combinations of different molar ratios at a constant [NaBr] = 10 mM were prepared[26] in stoppered test tubes and were equilibrated for two weeks in a water bath at 298 K.

Methods. ***NMR, Mass Spectra, Elemental Analysis.*** The ^1H NMR spectra of the bolaforms were taken in an AVANCE 300 MHz (BRUKER) spectrometer; observed chemical shift values (δ) are reported in parts per million (ppm). The elemental analyses were done in a Perkin-Elmer CHN Analyzer. High-resolution mass- spectrometric (HRMS) data were acquired by electrospray ionization (ESI) techniques, both in the positive and in the negative modes in a Q-tof Micro-Quadruple mass spectrophotometer (Micromass, U.K.).

Tensiometry. Surface tension was measured by the platinum ring detachment technique with a du Noüy tensiometer (Krüss, Germany). A concentrated solution of pure bolaforms or their mixtures with either SDS or CTAB (in water/10 mM NaBr solution, as the case may be) was added to a known volume of aqueous solutions or aqueous NaBr solutions (10 mM). After thorough mixing and temperature equilibration at 298 K (using a Neslab RTE-100, temperature controlled circulator water bath of accuracy = ±0.1 K), the surface tension was measured with an accuracy of $\pm 0.1\ mN\ m^{-1}$. Further details of measurements were described in our earlier publication.[34]

Isothermal Titration Calorimetry. An Omega ITC microcalorimeter of Microcal Inc. was used for the microcalorimetric measurements at 298 K. A Neslab RTE-100 water bath employed to circulate constant-temperature water at several degrees lower than that in the calorimetric cell surroundings wherein the internal device maintained the experimental temperature with an accuracy of ±0.01 K. Concentrated surfactant

(SDS, CTAB, bolaforms, and their mixtures) solutions (about 20 times their critical micelle concentration) were added in installments at equal time intervals (210 s) into 1.352 mL of 10 mM NaBr solution taken in the calorimeter cell under constant stirring (300 rpm) condition. The reference cell contained 1.6 mL of 10 mM NaBr solution. The heat of dilution of the amphiphile or mixed amphiphile solution at each step of addition was stored in the instrument software. The enthalpy of micellization was the difference between the initial and final asymptotes in the observed enthalpogram. For further details of the measurement protocol, we refer to our previous publications.[34,35]

Conductometry. Conductance measurements were taken in a Jenway conductometer with an accuracy of ±0.5% using a dip-type conductance cell of cell constant 0.1 cm^{-1}. The temperature of the solution (10 mM NaBr) was maintained at 298 K with a Neslab RTE-100 circulator water bath with an accuracy of ±0.1 K.[34]

Spectrophotometry. Absorption spectra of pure and mixed bolaform solutions at 298 K were recorded with a UV−vis 1601 spectrophotometer (Shimadzu) using a quartz cell of path length 1 cm.

Dye Solubilization. In this process, solubilization of a water insoluble, neutral dye, DPH,[36] into micellar and vesicular solutions was studied. Five microliters of THF solution of DPH (0.075 mM) was added both to 4 mL of 10 mM aquo-NaBr solution and to 4 mL of pure THF, and the absorption spectra of the prepared solutions were recorded after 24 h in a Shimadzu UV−vis 1601 spectrophotometer at 298 K. Various concentrations of mixed bolaform systems with a particular [bolaform]/[SDS] or [bolaform]/[CTAB] ratio and containing same concentrations of NaBr and DPH were also prepared and their absorption spectra were also recorded at the same temperature after 24 h of ageing. The analyzed results helped to understand the solubilization behavior of the self-aggregated assemblies of mixed bolaform−SDS and bolaform−CTAB systems.

Dye Entrapment/Encapsulation. The vesicular solutions of mixed bolaform−SDS and bolaform−CTAB systems of different concentrations were prepared in 0.5 mM aqueous bromophenol blue solution and aged at 298 K for 1 day prior to the experiment. A 0.35 mL aliquot of the mixture in each case was added slowly on the top of a 1 × 25 cm Sephadex G-50 (AR grade, Sigma) gel column, and then eluted with 10 mM NaBr solution at a very slow rate (0.25 mL min^{-1}). The released fractions were collected in separate test tubes, and their optical densities were measured in a Shimadzu UV−vis 1601 spectrophotometer at 592 nm. The elution process was carried out until the absorbances of the collected samples became practically zero.[26,37]

Dynamic Light Scattering. A BI-200SM Goniometer (Ver. 2.0) of Brookhaven Instruments Co., Hottsville, NY, was used for dynamic light scattering (DLS) measurements at 298 K. Light of 632 nm from a He−Ne laser (22 mW) was used as the incident beam. The measurements were conducted at a scattering angle of 90°. All the solutions were filtered several times through a cellulose acetate membrane filter of pore size 0.45 μm before the measurements. The diffusion coefficients (D) of the dispersed colloidal bolaforms were determined in the instrument and the apparent hydrodynamic radii (R_h) were deduced from Stokes−Einstein equation $R_h = k_B T/6\pi\eta D$ for spherical particles, where k_B and η represent the Boltzmann constant and the solvent viscosity, respectively, and T is the absolute temperature. For further details, we refer to our earlier publication.[38]

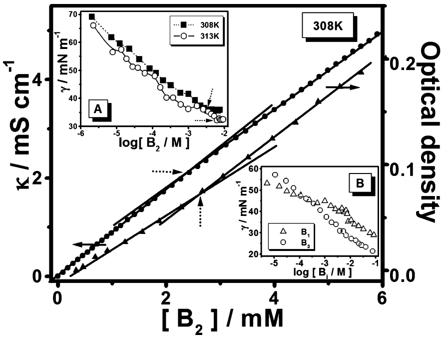

Figure 1. Determination of CMC of B_2 in aqueous medium. Main diagram: ●, conductometry; ▲, spectrophotometry at 308 K. CMC points are indicated by broken arrows. Inset A: tensiometric plots of B_2 in aqueous medium. Inset B: tensiometric profiles of B_1 and B_3 in aqueous medium at 308 K.

Results and Discussion

1. Physicochemical Behavior of Pure Bolaforms. ***A. Self-Assembly Formation in Aqueous Medium.*** The aqueous solubility of bolaforms followed the order $B_1 \approx B_3 \gg B_2$. B_1 and B_3 have strong hydrophilic groups at both ends of the methylene chain to make them water-soluble, whereas B_2 has a single hydroxyl group at one end that causes reduction in solubility. All three bolaforms have a common trimethylammonium end group.

The tensiometric results for B_1 and B_3 in aqueous solution showed no break (although surface tension (γ) values for both decreased with concentration), implying the absence of self-aggregation (i.e., micelle formation) in aqueous medium up to reasonably high concentrations,[22,23] or if there is self-aggregation, it must be greater than 100 mM (Figure 1, inset B). The conductometric and spectrophotometric experiments also supported the tensiometric results of no transitions in their concentration dependent courses. For bolaforms, the spacer, nature of the head groups, solvent, and the temperature are factors responsible for self-assembly.[4] They were not conducive for B_1 and B_3. Similar results were also reported earlier.[22−24] B_2 also did not show any concentration dependent transition at temperatures below 308 K, but sharp breaks were obtained at higher temperatures ($T \geq 308$ K) in tensiometric, conductometric, and spectrophotometric experiments (Figure 1, main diagram and inset A). The CMC values realized by the three methods were comparable. This led us to conclude that self-assembly of B_1 and B_3 in aqueous medium was impracticable under the present conditions of measurements whereas B_2 formed micelles at $T \geq 308$ K. Comparable temperature dependent micellization processes for triblock copolymers [poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide)] of PPO/PEO ratios (0.19−1.79) are found in the literature.[36] The average CMC of B_2 increased with temperature (2.55 and 6.00 mM at 308 and 313 K, respectively). The above apparent irregular results may be attempted to rationalize in the following way. The nonpolar part of the amphiphile remained surrounded by "water-cage" ("iceberg") by way of hydrophobic hydration (HH). At higher temperature (>303 K) the caging effect or HH became weak, allowing the related B_2 molecules to self-aggregate with a CMC of 2.55 mM. At 313 K, the CMC increased (6.0 mM), although a lower value was expected. The temperature effect on factors like water structure, kinetic energy, headgroup desolvation, etc. might have concertedly overridden the decreased HH contribution and reversed the direction of the CMC change. Further studies are required to shed more light on this matter. However, since ionic surfactants show a

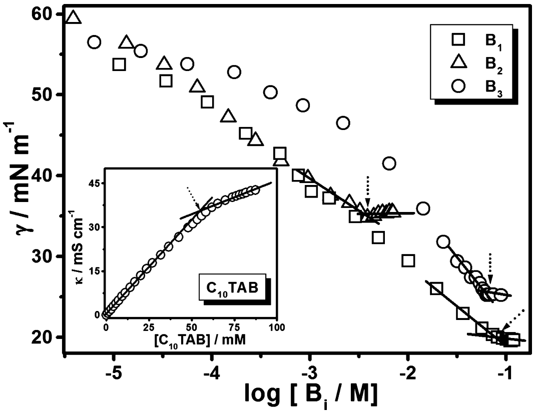

Figure 2. Tensiometric profiles of bolaforms in 10 mM NaBr solution at 298 K. Main plot: □, B_1; Δ, B_2; ○, B_3. CMC points are indicated by broken arrows. Inset: conductometric determination of CMC of $C_{10}TAB$ in 10 mM NaBr solution at 298 K.

minimum in the CMC−temperature plot, the increase in CMC with increasing temperature is possible.[39] The results also do not corroborate with the existing knowledge that in bolaforms, the length of spacers equivalent to sixteen or more carbon atoms is required for them to self-associate.[23,24] The above observations warrant further research. The fluctuating γ value as a function of concentration for B_2 at temperatures ≥308 K (Figure 1, inset A) up to the CMC point was an unexpected behavior.[22] It implied that the adsorption of B_2 at the air/water interface did not reach a stable state until the amphiphile concentration attained CMC.

B. Self-Aggregation in 10 mM NaBr Solution. Salts generally have a CMC decreasing effect,[39] the ionic amphiphiles are perceptibly affected; the nonionics and zwitterionics are weakly affected. A large CMC reduction of hexadecyltrimethylammonium bromide and its analogues in the presence of salt has been reported in literature.[40] All the bolaforms were found to form micelles in 10 mM NaBr solution at 298 K. Their tensiometric profiles were smooth. The average CMCs of B_1, B_2, and B_3 by different methods were 66.7, 5.12, and 63.5 mM, respectively, at 298 K (Figure 2, main plot). In 10 mM NaBr, the analogous $C_{10}TAB$ formed CMC at 54.0 mM at 298 K (Figure 2, inset). From the CMC formation point of view, B_1 and B_3 were more hydrophilic than $C_{10}TAB$. Like in aqueous medium, the CMC formed in salt medium by conductometry and spectrometry fairly agreed with tensiometry (e.g., in 10 mM NaBr, the CMC values for B_2 obtained by tensiometry, conductometry, and spectrophotometry at 298 K were 5.15, 5.10, and 5.11 mM, respectively). It may be added that along with the transition points in the plot (Figures 1 and 2) to locate CMCs, the procedure of second and third derivatives of the measured concentration dependent physical properties were also used.[41] All these results were in close agreements. A typical illustration is presented in Figure 3 for equimolar mixtures of B_2 and SDS to witness applicability of the derivative plots both for CMC and for CVC (subsequently discussed in section 3). The reported average CMC and CVC values were, thus, fairly accurate.

2. Interaction of Bolaforms with SDS and CTAB. The interaction between the bolaforms and the conventional surfactants, SDS and CTAB were studied at 298 K by conductometry and microcalorimetry. The aqueous solutions of B_1 and B_2 (0.5 mM) were titrated with SDS, and B_3 (0.5 mM) was titrated with both SDS and CTAB since B_3 was zwitterionic. The conductometric and microcalorimetric results were comparable (Figure 4, main plot). The results are summarized in Table 1. As per expectation, while titrating with SDS, B_1 produced the first break at 2:1 mole ratio ([SDS]/[B_1]), whereas both B_2 and B_3 produced the first breaks at about 1:1 mole ratio. Likewise, the calorimetric and conductometric titrations of B_3 with CTAB produced breaks at 1:1 mole ratio (Figure 4, inset). The products were totally or partially charged or neutralized species. It is seen in Figure 4 (main plot) that for B_1−SDS, after the first break (at [SDS]/[B_1] ≈ 2), a second break appeared at a mole ratio of 5.42. Similar second breaks were also observed in both B_3−SDS and B_2−SDS systems (Table 1). The second break stood for association of the formed ion pairs in solution with excess SDS to yield mixed micelles. For B_3−CTAB systems, only a single break at 1:1 mole ratio was observed. The second breaks occurred at SDS to bolaform mole ratios of 5.42, 5.3, and 5.5 for B_1, B_2, and B_3, respectively; they corresponded to the [SDS] of 2.71, 2.65, and 2.75 mM, respectively. The observed CMCs of SDS and CTAB at 298 K in the presence of 10 mM NaBr were at 6.76 and 0.87 mM, respectively. The CMC_{mix} values were much lower than the CMC of SDS, indicating the formation of mixed micelles. B_3 (0.5 mM) required ~0.5 mM CTAB solution for the neutralization of its carboxylate end. The product was a quaternary salt having appreciable solubility not to form mixed micelle easily even by the addition of excess CTAB.

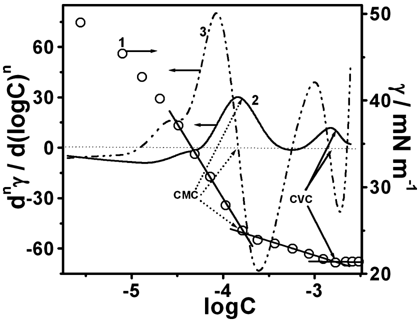

Figure 3. Representative normal and derivative plots of tensiometric profile of equimolar mixture of B_2 and SDS at 298 K. Symbols: 1, normal tensiometric plot; 2, second derivative plot; 3, third derivative plot. CMCs (mM): CMC (1), 0.147; CMC (2), 0.139; CMC (3), 0.137; CMC_{ave}, 0.141. CVCs (mM): CVC (1), 1.60; CVC (2), 1.51; CVC (3), 1.56; CVC_{ave}, 1.56.

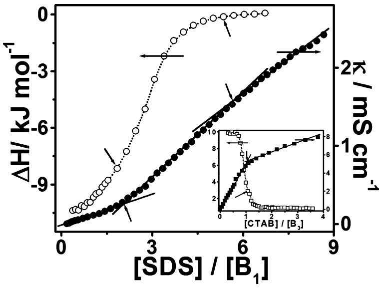

Figure 4. Conductometric and microcalorimetric titration of B_1 by SDS at 298 K. Break points are shown by solid arrows. Main diagram: conductometry (●) and microcalorimetry (○). Inset: conductometric (■) and microcalorimetric (□) titration of B_3 by CTAB at 298 K.

TABLE 1: Results of Conductometric and Microcalorimetric Titration of Bolaforms[a] by SDS and CTAB at 298 K

	break point molar ratios			
method	[SDS]/[B_1]	[SDS]/[B_2]	[SDS]/[B_3]	[CTAB]/[B_3]
conductometry	2.01, 5.57	1.09, 5.30	0.90, 5.52	1.00
microcalorimetry	1.92, 5.27	1.10, 5.27	1.08, 5.90	0.92
mean	1.97, 5.42	1.10, 5.29	0.99, 5.71	0.96

[a] Concentrations of bolaforms used = 0.5 mM.

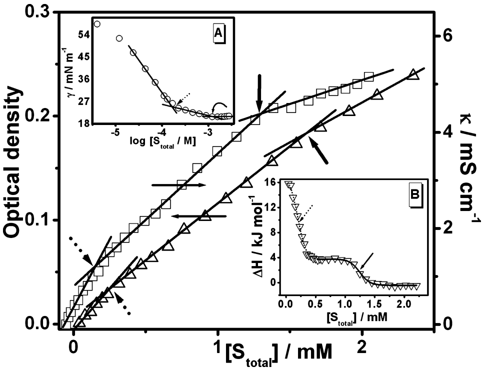

Figure 5. Determination of CMC of mixed bolaform−SDS systems at 298 K. CMC$_{mix}$ and CVC are indicated by broken and bent arrows, respectively. Main diagram: conductometry (□) and spectrophotometry (Δ). Inset A: tensiometry (○). Inset B: microcalorimetry (▽). Systems: □, B$_2$−SDS (3:1); Δ, B$_2$−SDS (1:1); ○, B$_2$−SDS (3:1); ▽, B$_2$−SDS (2:3).

3. Behavior of Bolaforms Mixed with Either SDS or CTAB in 10 mM NaBr Solution. ***A. Interfacial and Bulk Phenomena.*** The bolaforms formed clear solutions when mixed with oppositely charged surfactants in varied molar ratios in 10 mM aqueous NaBr solution. Throughout the measurements, [NaBr] was maintained at 10 mM. In the literature, oppositely as well as similarly charged surfactants of widely varied alkyl chains as in bolaforms can be found.[16,26] Herein we use surfactants of mild to moderately varied alkyl chains to interact with the bolaforms. The tensiometric profiles of mixed B$_1$−SDS and B$_2$−SDS systems produced two transitions at 298 K (Figure 5, inset A). Formation of two types of aggregates was envisaged.[26] The first break corresponded to the critical mixed micelle concentration (CMC$_{mix}$) whereas the second represented the critical vesicle concentration (CVC).[26,42] The locations of the breaks depended on the bolaform: SDS mole ratio. In the case of B$_1$−SDS, two transitions occurred up to $\alpha_{B_1} = 0.40$. For the B$_2$−SDS system, two transitions appeared up to $\alpha_{B_2} = 0.75$. The systems B$_3$−SDS and B$_3$−CTAB only produced a single transition at all the mole ratio compositions. The first transition (CMC$_{mix}$) values followed a sigmoidal trend with α_{B_3} in the mixture. The results of the three systems are presented in Table 2−4. The transition points presented and discussed above were the average values obtained by tensiometry, microcalorimetry (Figure 5, inset B), conductometry (Figure 5, main plot), and spectrophotometry (Figure 5, main plot). The interfacial adsorptions of the bolaforms and their combinations with SDS and CTAB were estimated using the Gibbs adsorption equation.[41] Thus,

$$\Gamma_{\max} = \frac{-1}{2.303nRT} \lim_{C \to \mathrm{CMC}} \left(\frac{\mathrm{d}\gamma}{\mathrm{d}\log C} \right) \tag{1}$$

where $\Gamma_{\max}$ (in mol m^{-2}) is the maximum surface excess at CMC, C stands for the total concentration of the pure or mixed surfactant in M, n is the effective number of chemical species (ions) present in solution, R is the universal gas constant, and T is the absolute temperature. The value of n in the binary mixtures of surfactants herein considered was obtained from the following rationale. For B$_1$, B$_2$, and B$_3$, the number of species formed by way of dissociation were 2, 2, and 3, respectively. The SDS and CTAB produced two species each. The n in a binary mixture of surfactants with stoichiometric mole fractions α_A and α_B producing a and b number of species, respectively can be found from the general formula[43]

$$n = a\alpha_A + b\alpha_B \tag{2}$$

For B$_1$−SDS mixtures, then, $n = 2\alpha_{B_1} + 2\alpha_{SDS} = 2$; for B$_2$−SDS mixtures, $n = 2\alpha_{B_2} + 2\alpha_{SDS} = 2$; and for B$_3$−SDS or B$_3$−CTAB mixtures, $n = 3\alpha_{B_3} + 2\alpha_{SDS}$ or $3\alpha_{B_3} + 2\alpha_{CTAB} = \alpha_{B_3} + 2$. In this scheme, the contribution of the added salt (10 mM NaBr) was not considered.

The $\Gamma_{\max}$ values are in Tables 2−4. For B$_1$−SDS mixed systems, the order of $\Gamma_{\max}$ obtained in terms of $\alpha_{B_1}$is 0.333 > 0.667 > 0.2 > 0.75 > pure SDS > pure B$_1$. Increase in $\Gamma_{\max}$ suggested that the packing at the air/water interface for the binary systems was enhanced more than that of the pure components. Tomasic et al.[44] reported a higher $\Gamma_{\max}$ for the equimolar mixture of CTAB and SDS systems than for the pure species. For B$_2$−SDS systems, the 1:1 ratio (charge-neutralized composition) produced the minimum $\Gamma_{\max}$. It was even less than that of SDS, indicating loose packing of the ion pairs at the interface. The equimolar combination of B$_3$−SDS was moderately larger than the pure components. On the other hand, the B$_3$−CTAB system showed a maximum $\Gamma_{\max}$ at 1:1 ratio with the following order: 0.5 > 0.667 > 0.75 > 0.333 > pure CATB ≈ pure B$_3$.

The minimum area of exclusion per surfactant molecule at the air/solution interface, $A_{\min}$ (nm^2 molecule^{-1}) was obtained from the relation[45]

$$A_{\min} = 10^{18}/N_A\Gamma_{\max} \tag{3}$$

where N_A is Avogadro's number. The $A_{\min}$ values are in Tables 2−4. The $A_{\min}^{SDS}$ value was less than that of the bolaforms. The $A_{\min}^{CTAB} \approx A_{\min}^{B_3}$ condition implied that both B$_3$ and CTAB had comparable interfacial occupancies.

The parameter, pC_{20} is a measure of the surface activity[45] of a surfactant (pC_{20} = −log C_{20}, where C_{20} denotes the concentration of the surfactant in mol dm^{-3} needed to reduce the surface tension of pure solvent by 20 mN m^{-1}). The higher the pC_{20} value, greater is the surface activity of the surfactant. According to this rationale and results in Tables 2−4, the herein studied systems produced the following efficiency order: CTAB > SDS ≈ B$_2$ > B$_1$ > B$_3$. All the mixed bolaform systems with SDS were more surface active than their parent components. The B$_3$−CTAB mixed systems were less surface active than CTAB but fairly greater surface active than B$_3$.

Microcalorimetric results (Figure 5, inset B) produced sharp breaks for the mixed bolaform systems, and the results were in good agreement with tensiometry. The sigmoidal part for the second transition evidenced vesicle formation. The derived parameters are in Tables 2 and 3. The enthalpy values for vesicle formation were all negative. The magnitudes for the B$_1$−SDS system were apparently greater than the B$_2$−SDS system. The composition dependent enthalpies for micelle and vesicle formation for both the systems were comparable. The scope for a detailed energetic study on the vesicle formation remains.

B. Energetics of Formation of Self-Assembled Species in 10 mM Aqueous NaBr Solution. The energetics of the assembled species formed in solution were assessed in the light of the pseudophase model. The standard Gibbs' free energies of micellization for both pure and mixed species were calculated from the relation[41,45,46]

$$\Delta G_m^0 = (1 + \beta)RT \ln x_T \tag{4}$$

where x_T is the average transition point values (CMC or CMC$_{mix}$) of the surfactant systems in mole fraction unit. In this calcula-

TABLE 2: Thermodynamic Parameters of B_1−SDS Mixed Systems[a,b,c] in 10 mM NaBr Medium at 298 K

α_{B_1}	$(CMC_{ave})_m$ $(CVC_{ave})_v$	$10^6\ \Gamma_{max}\ (A_{min})$	$(-\Delta H^0_{cal})_m$ $(-\Delta H^0_{cal})_v\ [pC_{20}]$	$-\Delta G^0_m\ (-\Delta G^0_{ad})$	$X^M_{B_1}\ (X^\sigma_{B_1})$	$f^M_{B_1}\ (f^\sigma_{B_1})$	$f^M_{SDS}\ (f^\sigma_{SDS})$	$-\beta^M\ (-\beta^\sigma)$	$-\Delta G^M_E$
0	$(6.76)_m$	1.57 (1.06)	$(2.37)_m$ [3.17]	22.3 (41.0)					
0.2	$(0.575)_m$ $(0.814)_v$	2.25 (1.65)	$(12.0)_m$ $(3.93)_v$ [4.05]	28.4 (44.0)	0.39 (0.40)	0.004 (0.029)	0.109 (0.209)	14.6 (9.81)	8.32
0.333	$(0.354)_m$ $(0.864)_v$	2.62 (1.42)	$(-15.0)_m$ $(13.6)_v$ [4.35]	29.6 (44.2)	0.42 (0.43)	0.004 (0.035)	0.056 (0.149)	16.3 (10.3)	9.69
0.667	$(0.630)_m$	2.46 (1.52)	$(1.53)_m$ [4.02]	28.2 (43.5)	0.46 (0.49)	0.014 (0.085)	0.045 (0.103)	14.7 (9.48)	8.49
0.75	$(0.884)_m$	2.08 (1.79)	[4.67]	27.4 (43.4)	0.47 (0.50)	0.024 (0.106)	0.048 (0.106)	13.7 (8.98)	7.70
1	$(66.7)_m$	0.94 (3.99)	[3.08]	16.7 (58.4)					

[a] CMC/CVC, Γ_{max}, A_{min}, and (ΔH^0_{cal}, ΔG^0_m, ΔG^0_{ad}, and ΔG^M_E) are expressed in mM, mol m^{-2}, nm^2 molecule^{-1}, and kJ mol^{-1} units, respectively. [b] Both CMC and ΔH^0_{cal} have two values for a single binary composition at different α_{B_1}. The first transition represents critical concentration for mixed micelle formation (CMC_{mix}) and the second one represents critical concentration for vesicle formation (CVC). [c] In columns 2 and 4, micelle and vesicle parameters are presented with subscript m and v, respectively.

TABLE 3: Thermodynamic Parameters of B_2−SDS Mixed Systems[a,b,c] in 10 mM NaBr Medium at 298 K

α_{B_2}	$(CMC_{ave})_m$ $(CVC_{ave})_v$	$10^6\ \Gamma_{max}\ (A_{min})$	$(-\Delta H^0_{cal})_m$ $(-\Delta H^0_{cal})_v\ [pC_{20}]$	$-\Delta G^0_m\ (-\Delta G^0_{ad})$	$X^M_{B_2}\ (X^\sigma_{B_2})$	$f^M_{B_2}\ (f^\sigma_{B_2})$	$f^M_{SDS}\ (f^\sigma_{SDS})$	$-\beta^M\ (-\beta^\sigma)$	$-\Delta G^M_E$
0	$(6.76)_m$	1.56 (1.06)	$(2.37)_m$ [3.17]	22.3 (41.0)					
0.333	$(0.139)_m$ $(0.735)_v$	2.27 (0.73)	$(-3.99)_v$ [4.45]	32.0 (47.5)	0.49 (0.44)	0.018 (0.021)	0.025 (0.091)	15.4 (12.4)	9.28
0.4	$(0.219)_m$ $(1.01)_v$	1.79 (0.93)	[4.39]	30.8 (50.4)	0.5 (0.45)	0.034 (0.024)	0.034 (0.083)	13.5 (12.3)	8.16
0.5	$(0.153)_m$ $(1.60)_v$	1.42 (1.17)	$(8.45)_m$ $(4.87)_v$ [4.43]	31.7 (52.7)	0.51 (0.47)	0.029 (0.016)	0.022 (0.039)	14.7 (14.7)	9.04
0.667	$(0.151)_m$ $(0.374)_v$	2.07 (0.80)	$(1.56)_m$ $(1.29)_v$ [4.38]	31.8 (47.9)	0.53 (0.49)	0.037 (0.039)	0.015 (0.050)	14.9 (12.5)	9.05
0.75	$(0.154)_m$ $(1.58)_v$	2.27 (0.73)	$(3.91)_m$ $(1.01)_v$ [4.32]	31.7 (46.8)	0.55 (0.5)	0.041 (0.055)	0.008 (0.055)	15.8 (11.6)	8.99
0.833	$(0.242)_m$	1.72 (0.96)	[4.46]	30.6 (51.6)	0.56 (0.52)	0.07 (0.044)	0.014 (0.025)	13.7 (13.6)	7.86
1	$(5.12)_m$	0.66 (2.50)	[3.15]	23.0 (61.0)					

[a] CMC/CVC, Γ_{max}, A_{min}, and (ΔH^0_{cal}, ΔG^0_m, ΔG^0_{ad} and ΔG^M_E) are expressed in mM, mol m^{-2}, nm^2 molecule^{-1}, and kJ mol^{-1} units, respectively. [b] Both CMC and ΔH^0_{cal} have two values for a single binary composition at different α_{B_1}. The first transition represents critical concentration for mixed micelle formation (CMC_{mix}) and the second one represents critical concentration for vesicle formation (CVC). [c] In columns 2 and 4, micelle and vesicle parameters are presented with subscript m and v, respectively.

tion, the contribution of β (fraction of counterions bound to the micellar species) was neglected since it was small (<5%). For normalization of results, in the calculations of ΔG^0_m of pure SDS and CTAB (in 10 mM NaBr solution), their β values were also not used.

The energetic and related parameters are presented in Tables 2−4. They evidenced that the free energy changes for the mixed micellar systems of B_1−SDS and B_2−SDS systems were more spontaneous than the pure systems; for the B_3−CTAB system, they were comparable with pure CTAB and more spontaneous than B_3. Except for two cases (α_{B_1} and $\alpha_{B_2} = 0.333$) the enthalpy changes for mixed micelle and mixed vesicle formation were found to be exothermic and dependent on the system composition (Tables 2 and 3). The enthalpy changes for the mixed micelle formation for both B_1−SDS and B_2−SDS systems with respect to their stoichoimetric ratios fitted to tertiary polynomial equations with $R^2 = 1$. The mixed vesicle formation was less spontaneous than mixed micelle formation.

The standard free energy of interfacial adsorption (ΔG^0_{ad}) at CMC or CMC_{mix} was estimated from the relation,[46]

$$\Delta G^0_{ad} = \Delta G^0_m - \left(\frac{\pi_{CMC}}{\Gamma_{max}}\right) \tag{5}$$

TABLE 4: Thermodynamic Parameters of B_3−CTAB and B_3−SDS Mixed Systems[a] in 10 mM NaBr Medium at 298 K

α_{B_3}	CMC_{ave}	$10^6\ \Gamma_{max}$ (A_{min})	pC_{20}	$-\Delta G^0_m$ ($-\Delta G^0_{ad}$)	$X^M_{B_3}$ ($X^\sigma_{B_3}$)	$f^M_{B_3}$ ($f^\sigma_{B_3}$)	f^M_{SDS} (f^σ_{SDS})	$-\beta^M$ ($-\beta^\sigma$)	$-\Delta G^M_E$
				B_3−CTAB					
0	0.87	1.20 (1.39)	4.90	27.4 (56.3)					
0.333	1.02	1.04 (1.58)	4.00	27.0 (59.0)	0.15 (0.41)	0.035 (0.001)	0.901 (0.026)	4.61 (21.6)	1.20
0.5	1.23	1.56 (1.06)	4.47	26.6 (47.6)	0.19 (0.41)	0.050 (0.003)	0.849 (0.057)	4.54 (17.0)	1.16
0.667	1.87	1.34 (1.24)	4.38	25.5 (51.0)	0.19 (0.43)	0.100 (0.005)	0.883 (0.046)	3.46 (16.6)	0.12
0.75	2.69	1.08 (1.54)	4.58	24.6 (56.2)	0.18 (0.45)	0.176 (0.002)	0.920 (0.017)	2.58 (20.1)	−0.89
1	63.5	1.18 (1.40)	2.06	16.8 (45.5)					
				B_3−SDS					
0.5	5.25	1.20 (1.08)	3.47	23.0 (38.9)	0.34 (0.32)	0.121 (0.045)	0.571 (0.503)	4.84 (6.72)	2.52

[a] CMC/CVC, Γ_{max}, A_{min}, and (ΔH^0_{cal}, ΔG^0_m, ΔG^0_{ad}, and ΔG^M_E) are expressed in mM, mol m^{-2}, nm^2 $molecule^{-1}$, and kJ mol^{-1} units, respectively.

where π_{CMC} ($\gamma_0 - \gamma_{CMC}$ or $\gamma_0 - \gamma_{CMC_{mix}}$) is the surface pressure at CMC or CMC_{mix}; γ_0, γ_{CMC}, and $\gamma_{CMC_{mix}}$ are the surface tension values of 10 mM NaBr solution, pure and mixed surfactant solutions, respectively, at their respective transitions.

The change in free energies due to self-aggregation in the bulk micelle formations and other transitions suggested that they were much less spontaneous than amphiphile adsorption at the interface, i.e., $\Delta G^0_{ad} \ll \Delta G^0_m$. The order of magnitudes of ΔG^0_{ad} for the B_1−SDS mixed system was pure B_1 > mixed B_1−SDS > pure SDS. Effectively, the ΔG^0_{ad} values only mildly varied with solution composition in the mixed surfactant systems. Similar was the observations on B_2−SDS and B_3−SDS systems. The B_3−CTAB mixed systems showed ΔG^0_{ad} values to be more negative than pure B_3 compared to other binaries. For B_3−CTAB systems, there was no composition dependent trend in ΔG^0_{ad}.

C. Assessment of Mutual Interaction of Bolaforms with SDS and CTAB in the Micelle and at the Interface. The compositions of mixed surfactants in micelles in the bulk as well as in the adsorbed monolayer at the interface are usually different from their stoichiometric compositions.[47,48] The interaction between the species in the bulk and at the interface can be reasonably studied in the light of regular solution theory (RST) of Rubingh[49] and the theory of Rosen,[50,51] respectively. The RST, based on thermodynamic principle, is capable of predicting the synergistic as well as antagonistic interaction between the amphiphiles in mixed micelles, and the micellar composition along with their activity coefficients. The theory of Rosen provides similar information on the interaction at the air/solution interface. Rubingh's theory of interaction between binary mixtures of bolaform with conventional surfactant in solution has been used by different workers.[16,52] Their interactions at the interface as schemed in Rosen's theory has scarcely (if ever) done in the past. The theories are simple and reasonably informative on the mixed interacting amphiphile systems. We have used the Rubingh and Rosen models to investigate the mixed systems of bolaforms with both SDS and CTAB. The Rubingh's model (RM) deals with mixed systems based on nonideality and several reasonable approximations.[49−51] The CMC_{mix} of a binary mixture of surfactants with activity coefficients f_1 and f_2, respectively, can be expressed by the following relation,

$$\frac{1}{CMC_{mix}} = \frac{\alpha_1}{f_1 CMC_1} + \frac{\alpha_2}{f_2 CMC_2} \qquad (6)$$

where α_1 and α_2 are the mole fraction of surfactants 1 and 2, respectively in the solution; CMC_1 and CMC_2 are the critical micelle concentrations of surfactants 1 and 2, respectively. The above equation is a modified form of Clint's equation[53] for ideal mixture wherein the activity coefficients ('f' terms) are taken to be unity so that $1/CMC_{mix} = \alpha_1/CMC_1 + \alpha_2/CMC_2$.

The average CMC_{mix} values herein observed were lower than those calculated from the above relation of Clint. The negative deviation from the ideal equation followed the order B_2−SDS > B_1−SDS > B_3−SDS > B_3−CTAB at a given mole fraction composition. The mixed systems were all synergistic.

The micellar compositions ($X^M_{B_i}$ and X^M_{SDS} or X^M_{CTAB}), the activity coefficients ($f^M_{B_i}$ and f^M_{SDS} or f^M_{CTAB}) of the binary components and the interaction parameter β^M (synergistic or antagonistic) has been calculated from RM,[49] and the relations used for the estimations can be found in the literature.[47,48,54−56] These are not presented to save space; only the results are shown in Tables 2−4.

Using Rosen's rationale (RR)[50,51] and the measured surface tension of mixed surfactants, the composition of bolaforms and SDS or CTAB in the mixed monolayer, their surface activity coefficients ($f^\sigma_{B_i}$and f^σ_{SDS} or f^σ_{CTAB}), and the interaction parameter (β^σ) were calculated. The constant level of the surface tension (γ) was arbitrarily chosen at $\gamma = 38$ mN m^{-1} sufficiently below their respective CMCs.[54,55] The mole fraction of the components in the mixed monolayer ($X^\sigma_{B_i}$ and X^σ_{SDS} or X^σ_{CTAB}) were evaluated using the molar solution concentrations of the individual surfactants and their mixtures required to have the same value of γ (38 mN m^{-1}). The data treatment rationale is comparable with Rubingh's treatment.[49] The results by the RR model are also presented in Tables 2−4.

The $X^M_{B_1}$ values in B_1−SDS combinations varied between 0.39 and 0.47; thus, SDS contributed more in the mixed micellar phase than B_1. For the B_2−SDS systems, B_2 dominated in the mixed micellar phase ($X^M_{B_2}$varied from 0.49 to 0.6) whereas in the 1:1 B_3−SDS system, SDS again contributed more than the bolaform, B_3 ($X^M_{SDS} = 0.66$). On the other hand, in the B_3−CTAB system, $X^M_{B_3} \ll X^M_{CTAB}$, the former ranged only between 0.15 and 0.19. The varied physicochemistry of the mixed systems were thus realized.

The $f^M_{B_1}$ values in the mixed micelles of B_1−SDS hardly varied with α_{B_1} and that of SDS decreased with increasing α_{B_1} (range 0.109−0.045). For the B_2−SDS system, the $f^M_{B_2}$ for the mixed micelles were also small (varied between 0.07 and 0.041). The activity coefficients of SDS in the mixed B_2−SDS system did not vary much (0.008−0.034). The $f^M_{B_3}$ value for the B_3−CTAB mixed system increased with increasing α_{B_3} (fitted to a secondary polynomial equation with $R^2 = 0.985$) whereas those for SDS were close to unity, though less than unity for both components. The $f_{B_3}^{M}$ value (0.121) in the 1:1 B_3−SDS system was smaller than that of SDS (0.571).

The mole fraction of all the bolaforms in the mixed monolayers ($X_{B_i}^{g}$) mildly increased with increasing α_B. The bolaforms (B_1 and B_2) and SDS almost equally contributed to the mixed monolayer formation. The B_3 and CTAB also contributed nearly equally to the mixed monolayer, the contribution of SDS in the B_3−SDS system was much greater. The activity coefficients of all the bolaforms in the mixed monolayer were small and mildly increased with α_B for the B_1−SDS system. No such ordering in the value of $f_{B_2}^{g}$ was observed for the B_2−SDS system. However, the $f_{B_3}^{g}$ values in the mixed B_3−CTAB monolayer were practically nonvariant. For the B_1−SDS and B_3−CTAB systems, the maximum f_{SDS}^{g} values arose at the charge- neutralized condition.

D. Synergism in Mixed Micelle Formation. The signs and magnitudes of β^M and β^σ tell about the types of interaction and their extents. The necessary conditions for synergistic interaction[47,48,51,54] are (1) β^M and β^σ must be negative, and (2) $|\beta^M| > |\ln(CMC_1/CMC_2)|$and $|\beta^\sigma| > |\ln(C_1^0/C_2^0)|$. Here CMC_1 and CMC_2 are the CMCs of component 1 and component 2, respectively, and C_1^0 and C_2^0 are the molar concentrations of the first and second surfactants, respectively, in the bulk phase required to produce the same γ in both the systems. The β^M and β^σ values found in the mixed bolaform−SDS and mixed bolaform−CTAB systems were negative. The second condition of greater magnitude of β^M values than the ln(CMC ratio) or β^σ values than the ln(concentration ratio) at equal γ also was in favor of synergism. Similar synergistic interactions are also found in the literature.[54,55] According to Rosen et al.,[54] $|\beta^M| > |\beta^\sigma|$ should be the condition for synergism. In this study, this condition was found to hold for B_1−SDS and B_2−SDS systems; both B_3−SDS and B_3−CTAB evidenced $|\beta^M| < |\beta^\sigma|$. Clint[56] has shown that the above-mentioned Rosen[54] criterion cannot be a generalization for synergism. The essential condition has to be $\beta < 0$, which was true for all the mixed systems herein studied. The β^M values for B_1−SDS were fitted to a secondary polynomial equation with α_{B_1} ($R^2 = 0.969$) showing a maximum at the charge neutralization ratio, the β^M values with α_{B_2} for the B_2−SDS system did not produce a proper trend. The 1:1 B_3−SDS system yielded a fair negative β^M value (−4.84). The B_3−CTAB combinations yielded mixed CMCs lower than B_3 but greater than CTAB. Their negative β^M values (ranged between −2.58 and −4.61) also suggested fair synergism in the mixed micelles. The values fitted to a secondary polynomial equation with respect to α_{B_3}, yielding $R^2 = 0.999$. Synergistic interaction of cationic bolaform with SDS and sodium laurate[16] produced β^M values −10.9 and −7.2, respectively. Such interaction between a nonionic bolaform with two aza-crown ether head groups and SDS[52] yielded $\beta^M = -7.6$. The interactions were stronger for the herein studied systems.

For B_1−SDS systems, β^σ was found to fit to a secondary polynomial equation ($R^2 = 0.992$) with respect to α_{B_1}; for the B_3−CTAB system, a perfect fitting ($R^2 = 1$) to a tertiary polynomial equation was found with respect to α_{B_3}. For the mixed B_2−SDS system, the maximum synergism in the monolayer arose at the equimolar composition.

E. Excess Free Energy of Mixed Micellization and Mixed Monolayer Formation. The mutual interaction between the components of the mixed micelles was analyzed in terms of the excess free energy of micellization (ΔG_E^M), using the following relation,[57]

$$\Delta G_E^M = \Delta G_{m,\,mix}^0 - X_{B_i}^M \Delta G_{m,B_i}^0 - X_{SDS}^M \Delta G_{m,SDS}^0 \qquad (7)$$

The results are presented in Tables 2−4. The ΔG_E^M for both B_1−SDS and B_2−SDS were fairly negative compared with those for B_3−SDS and B_3−CTAB systems (at $\alpha_{B_3} = 0.75$, the value was found to be positive). The synergistic interaction thus followed the order B_1−SDS ≈ B_2−SDS ≫ B_3−SDS > B_3−CTAB. This order of ΔG_E^M was more or less obeyed also for β^M, as discussed earlier.

4. Dynamic Light Scattering Results. The preliminary DLS results on bolaform−SDS and bolaform−CTAB mixed micelles and vesicles produced first hand information on their hydrodynamic dimensions and polydispersities.[58] The system wise magnitudes of the mean diameter (*d*) and the PDI (polydispersity index) are as follows:

(1) For the 1:2 B_1−SDS system: at 0.50 mM (>CMC_{mix}), $d = 220$ nm, PDI = 0.273; at 1.30 mM (>CVC), $d = 325$ nm, PDI = 0.300.

(2) For the 1:1 B_2−SDS system: at 0.50 mM (>CMC_{mix}), $d = 186$ nm, PDI = 0.317; at 2.40 mM (>CVC), $d = 325$ nm, PDI = 0.280.

(3) For the 1:1 B_3−SDS system: at 6.20 mM (>CMC_{mix}), $d = 216$ nm, PDI = 0.390.

(4) For the 1:1 B_3−CTAB system: at 1.85 mM (>CMC_{mix}), $d = 225$ nm, PDI = 0.346.

In the above, the system concentrations were greater than their corresponding CMC_{mix} and CVC values. At the studied bola:SDS and bola:CTAB ratios, both mixed micelles and vesicles were formed for systems 1 and 2 whereas systems 3 and 4 produced only mixed micelles. The results evidenced the types of sizes that the assemblies offered. Their polydispersities were reasonable and comparable. The vesicle sizes were obviously larger than the mixed micelles. More studies are required for confirmation and elaboration. From TEM measurements, Yan et al.[16,26] have reported vesicle dimensions in the range 10−100 nm for mixed cationic bolaform−SDS and anionic bolaform−DTAB systems. The presently studied systems in the solution state have produced larger dimensions than the solvent removed samples examined by the above authors. Complementary studies by DLS and TEM are therefore required for better information on vesicle morphology and size.

5. Dye Solubilization and Entrapment. The structural changes (formation of micelles and vesicles) of the mixed bolaform and SDS or CTAB with increasing concentration can be supported from dye solubilization and dye entrapment experiments.[26,36] The neutral dye, DPH, was found to show spectral characteristics with a shoulder at 271 nm and three peak structures at 340, 355, and 375 nm in THF (dipole moment = 1.75D; dielectric constant = 7.58) (Figure 6, inset). In 10 mM aqueous NaBr solution DPH spectra showed a much reduced shoulder without the peaks at higher wavelengths. Increasing addition of the B_2−SDS mixture at 3:1 mol ratio evidenced the appearance of three characteristic peaks at 0.99 mM (fairly above its average $CMC_{mix} = 0.154$ mM, where solubilization of DPH in the interior of the mixed micelle occurred). At B_2−SDS concentrations of 1.79, 2.99, and 3.63 mM, the structural features of DPH became prominent with increasing absorbances (Figure 6, main diagram). The polarity of the aqueous salt solution was higher than that of THF, the interior of the micelles, and the molecular membrane of the vesicle,[26] where the dye molecules were located with comparable microenvironments.

The vesicles can entrap water-soluble dyes, drugs, etc. into their interior. We have used the water-soluble dye bromophenol

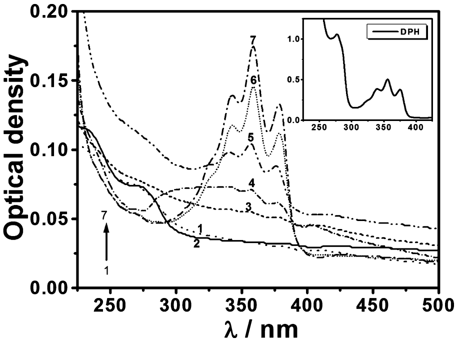

Figure 6. Shift of λ_{max} of DPH at different concentrations of B_2:SDS (3:1) at 298 K. [DPH] used = 0.09 μM. Main diagram: 1−7, mixed system of concentrations 0, 0.025, 0.09, 0.99, 1.79, 2.99, 3.60 mM, respectively. Inset: absorption spectra of DPH in THF at 298 K.

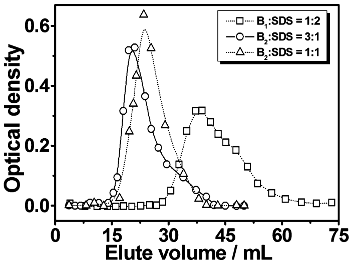

Figure 7. Elution profiles of mixed bolaform−SDS systems at 298 K. Systems: □, B_1−SDS (1:2); ○, B_2−SDS (3:1); Δ, B_2−SDS (1:1).

blue for such entrapment in the vesicles' aqueous interior. Addition of bolaform−surfactant (SDS or CTAB) mixtures at different mole ratios with a fixed concentration of the dye (9.4×10^{-8} M) on the top of a Sephadex (G-50) column produced elution profiles for B_1−SDS (1:2), B_2−SDS (3:1), and B_2−SDS (1:1) systems as depicted in Figure 7. The profiles for the B_1−SDS and B_2−SDS systems appear separated; the elution process was delayed in the latter. The symmetrical elution profiles with a single peak and without shoulder meant release of a single species (the vesicle-entrapped dye) from the column matrix. Interestingly, the same procedure followed on the B_3−CTAB system failed to elute out the vesicle from the column. Although this supported vesicle uptake in the Sephadex matrix, its nonelution remained to be explained.

6. Probable Structures at the Interface and Assemblies in the Bulk. The studied bolaforms (B_1, B_2, and B_3) and their combinations with both SDS and CTAB were expected to produce interesting species at the air/solution interface and in the bulk. Because of a short spacer (with ten methylene groups), it was expected (cf. Introduction) that their bending at the interface and in the aqueous bulk would not arise. But in 10 mM aqueous NaBr solution, the experimental results have produced interesting structural manifestations that are discussed below.

In Tables 2−4, the A_{min} values of the pure bolaforms and their combinations with SDS and CTAB are presented. The values followed the order B_1 (3.99 nm^2) > B_2 (2.50 nm^2) > B_3 (1.40 nm^2). This was because in B_1, both the hydrophobic groups are positively charged and hence repulsive force resulted in a higher area. In B_3, hydrophilic groups are oppositely charged and hence attractive to produce the lowest area. B_2 shows the intermediate value in A_{min} because one of hydrophilic groups is neutral. SDS and CTAB produced A_{min} values 1.06 and 1.39 nm^2, respectively. For their mixtures (with SDS for B_2 and B_3 at 1:1 molar ratio, and for B_1 at 1:2 molar ratio, and with CTAB for B_3 at 1:1 molar ratio), the order of A_{min} was parallel to the parent bolaforms, i.e., B_1−SDS (1.42 nm^2) > B_2−SDS (1.17 nm^2) > B_3−SDS (1.08 nm^2) ≈ B_3−CTAB (1.06 nm^2). The larger A_{min} values of the parent bolaforms than of SDS and CTAB suggested their wicket-like structures at the air/solution interface. In pure CTAB, repulsive interaction among the CTA^+ ions at the air/solution interface produced a larger A_{min} value than expected for a nonionic species. The combinations of bolaforms with SDS and CTAB produced A_{min} lower than their parent components (B_1, B_2, and B_3) because of charge neutralization. For quantification of results, detailed studies with rational modeling are warranted.

Bolaforms with large hydrophobic spacers form spherical micelles by way of folding the segments. In the case of shorter hydrophobic segments, such "folding up" becomes difficult and spherical micelles do not form. In this study, we have used bolaforms having a reasonably low hydrophobic segment. It was observed that they did not form micelles in the aqueous medium at around 298 K. It may be mentioned here that the "spacer length" criterion for the formation of micelle cannot be used on all kinds of bolaform surfactants.[59] However, in the presence of 10 mM NaBr in the aqueous medium, the herein studied bolaforms produced micelles. The structures of these micelles are, therefore, of importance. We believe that in the presence of electrolyte (10 mM NaBr), the "folding up" of the hydrophobic segment is possible to form spherical bolaform micelles in solution. But, the possibilities of formation of assemblies of "lamellar" as well as "stretched" conformations are also not ruled out.[60] A conclusive opinion on the assembly geometry cannot be given at present. To resolve the issue, more detailed studies are required. SDS and CTAB interacted with the bolaforms to form IPAs or catanionics, which became more hydrophobic to form both micelles and vesicles. Among all the studied combinations, B_3−SDS and B_3−CTAB formed only micelles but no vesicles, whereas the pairs B_1−SDS and B_2−SDS produced both micelles and vesicles. The B_2−SDS appeared to be more effective in this behavior. The factors like charge, solubility, and stoichiometry were considered vital for the types of assemblies to be formed in solution.

Conclusions

In aqueous medium, the doubly charged surface-active bolaforms (B_1 and B_3) do not show evidence for self-association within the studied temperature range 298−323 K, but the singly charged representative (B_2) forms micelles at $T \geq 308$ K. All the bolaforms, on the other hand, self-associate in 10 mM NaBr solution (i.e., in salt environment). The phenomenon is a contradiction to the existing experiences that bolaforms with hexadecyl or higher alkyl chain spacers can only form micelles in aqueous solution. The presently studied compounds have only decyl alkyl chains in the molecules. They form mixed micelles in combinations with both SDS and CTAB. The mixed systems are more surface active than their precursors. At higher concentrations, the mixed systems also produce vesicles. The B_1−SDS and B_2−SDS systems form mixed micelles and vesicles whereas B_3−SDS and B_3−CTAB systems form only mixed micelles. In the mixed micelles, the bolaforms show synergism with SDS and CTAB. In the B_1−SDS and B_2−SDS systems, the two components equally contribute to their aggregates composition. For the B_3−SDS and the B_3−CTAB systems, the contribution of B_3 in the aggregates is much less than both SDS and CTAB. However, their interfacial monolayers constitute nearly equal proportions of both the components (except 1:1 B_3−SDS system, where the contribution of

SDS is greater than that of B_3). Energetically, the interfacial adsorption is fairly more spontaneous than micelle formation, as expected. The mixed micelle and vesicle formation processes were found to be mostly exothermic, which decreased with increasing proportions of bolaform in the system. The distinct solubilization of the neutral dye, DPH, in the amphiphilic media suggested the existence of micelles and vesicles in them. The elution profile of bromophenol blue containing vesicle solution was found to be fairly sharp and symmetric; overlap with a simultaneous elution of the free dye was absent. The B_3−SDS and B_3−CTAB systems did not respond to the process for reasons unknown.

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